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EIGHTH QUARTERLY REPORT

February 1, 1951 to
April 30, 1951

on

A METALLURGICAL STUDY
OF MOLYBDENUM
(Contract No. N9cnr 82100,
Task Order No. N9onr 82101)

to

OFFICE OF NAVAL RESEARCH
NAVY DEPARTMENT

G-1332-1

BATTELLE
MEMORIAL INSTITUTE
505 King Avenue
COLUMBUS 1, OHIO

FORM 4?

Battelle Memorial Institute

July 26, 1951

Dr. I. R. Kramer
Head, Materials Branch
Office of Naval Research
Navy Department
Washington 25, D. C.

Dear Dr. Kramer:

<div align="center">

Contract No. N9onr 82100
Task Order No. N9onr 82101
Ref. No. NR 034-402
</div>

The Eighth Quarterly Status Report of research on molybdenum is attached herewith.

It has been found that a particular lot of molybdenum ages at room temperature when quenched from 3800°F. By means of internal-friction measurements, it is hoped to be able to identify the element responsible for aging.

The problem of evaluation of the ductility of molybdenum grows more complex as we identify additional significant factors. It now appears that, to account for all the variables known to influence the strain to fracture, it is necessary to include a description of the microstructure and the distribution of impurity elements, in addition to the commonly accepted (and more readily manipulated) variables, temperature, strain rate, stress system, and average composition.

The information on purity vs. ductility and on heat treatment vs. ductility is proving to be useful in the welding of molybdenum. Development work on welding has been going forward under other sponsorship. However, in anticipation of the modification in the terms of the recent contract extension, there will be, under this contract, more direct research on molybdenum welding in the ninth quarter.

Sincerely yours,

Robert M. Parke

RMP:jlw

STATUS REPORT

EIGHTH QUARTERLY REPORT

COVERING THE PERIOD FEBRUARY 1, 1951, TO APRIL 30, 1951

on

A METALLURGICAL STUDY OF MOLYBDENUM
(Contract No. N9onr 82100, Task Order No. N9onr 62101)
(Project NR 034-402)

to

OFFICE OF NAVAL RESEARCH
NAVY DEPARTMENT

BATTELLE MEMORIAL INSTITUTE
May 1, 1951

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EIGHTH QUARTERLY REPORT

COVERING THE PERIOD FEBRUARY 1, 1951, TO APRIL 30, 1951

on

A METALLURGICAL STUDY OF MOLYBDENUM
(Contract No. N9onr 82100, Task Order No. N9onr 82101)
(Project NR 034-402)

to

OFFICE OF NAVAL RESEARCH
NAVY DEPARTMENT

from

BATTELLE MEMORIAL INSTITUTE

May 1, 1951

SUMMARY

(Robert M. Parke)

A start has been made toward determining which elements impair
the ductility of cast molybdenum by ascertaining which elements are reduced
in concentration by the vacuum-fusion method. Nickel, manganese,
chromium, oxygen, hydrogen, and nitrogen concentrations are lowered by
vacuum fusion, while keeping carbon below 0.003 per cent. The next step
will be to add controlled quantities of selected elements to otherwise
high-purity molybdenum.

Samples of high-purity molybdenum, sufficiently large for
testing, have not been produced by reduction of molybdenum pentachloride.
Experimental difficulties are such that this method appears unattractive
in comparison with the vacuum-fusion method.

Gradient composition ingots in all the alloy systems to be tested for oxidation resistance have now been made. Thirty-eight of these ingots remain to be tested. Each of the alloys behaves differently during arc melting. The arc-melting characteristics of the various alloys are discussed in the report.

The program of high-temperature, creep-rupture testing to compare molybdenum from various sources has now been completed. Work has started to determine the effect of ambient atmosphere on the creep-rupture properties. The first tests are being made on wrought arc-cast molybdenum in a hydrogen atmosphere. Early results show somewhat greater ductility and lower rupture strength for the material tested in hydrogen as compared with that tested in vacuum. Preparations are being made to determine the effect of grain size, of preferred orientation, of impurities, and of processing variables on the creep-rupture properties at elevated temperatures.

The difficulties in measuring the solubility of oxygen in molybdenum have not yet been overcome. However, it is believed that the procedures described in this report will be successful up to 3000°F.

Quench aging has been shown to occur in molybdenum when quenched from 3800°F. Aging takes place at room temperature over a period of at least two months. This effect is important to the ductility studies, and so, experiments will be arranged to identify the element responsible for aging.

The ductility of molybdenum in the bend test can be roughly expressed by plotting the logarithm of the deflection rate against the reciprocal of the absolute temperature. Plots of this type have been made for wrought powder-metallurgy molybdenum and for as-cast arc-melted

molybdenum and will be made for as-cast high-purity molybdenum. If, through purification, cast molybdenum is found to be as ductile as wrought powder-metallurgy molybdenum by this method of ductility evaluation, then it will be assumed that the most promising means of obtaining a ductile molybdenum weldment is through control of impurities.

The internal-friction peak, tentatively identified at 575°F. in a sample of molybdenum containing 0.011 per cent carbon and quenched from 3800°F., could not be found in subsequent tests. Since these contradictory results could arise from aging effects, and since aging is itself important, subsequent internal-friction studies have been planned to discover which element causes aging. At room temperature and below room temperature, internal friction is linearly dependent on stress (at low stress amplitudes).

PREPARATION OF HIGH-PURITY MOLYBDENUM

HIGH-PURITY MOLYBDENUM BY VACUUM FUSION

(G. W. P. Rengstorff, H. B. Goodwin, and C. T. Greenidge)

Introduction

As described in prior reports, repeated vacuum arc melting of powder-metallurgy molybdenum produced cast molybdenum which did not exhibit the heretofore characteristic intergranular brittleness in a slow-bend test at room temperature. The vacuum-purified molybdenum also had a lower transition temperature and a higher critical strain rate than other, less pure, cast molybdenum.

The conclusion was reached that the improvement in ductility was the result of removal of an unknown impurity or impurities by volatilization and/or chemical reactions thermodynamically favored by low pressure.

The first step toward determining which element or elements impair the ductility of cast molybdenum was to ascertain which elements were reduced in concentration by the vacuum arc melting. Carbon, oxygen, nitrogen, and hydrogen were suspected. In the Seventh Report (page 333), the amounts of these elements in the two most ductile high-purity ingots which had been made at that time and in the melting stock were given. Oxygen and hydrogen were progressively lowered in three successive remeltings; carbon content was not changed and the precision of the analyses was not sufficient to permit any conclusions with respect to nitrogen.

The investigation has now been extended to determine the effect of vacuum arc melting on eight additional impurity elements and the effect of up to five remelts.

Experimental Work

A series of ingots was prepared by the vacuum arc-melting technique described on pages 239 to 243 of the Sixth Quarterly Report. These ingots were melted one to five times. The same powder-metallurgy melting stock was used to prepare all ingots. Each ingot and the melting stock were analyzed with as high precision as possible for the following elements:

Oxygen	(Vacuum-Fusion Method)
Hydrogen	Ditto
Nitrogen	Ditto
Carbon	(Combustion Method)
Sulphur	Ditto
Nickel	(Spectrographic Method)
Manganese	Ditto
Chromium	Ditto
Aluminum	Ditto
Silicon	Ditto
Copper	Ditto
Iron	Ditto

The results of the analyses are given in Table 31.

Most striking is the high sulphur* content of the melting stock and the fact that it was not lowered by repeated remelting.

Nickel, manganese, and chromium concentrations are shown to be lowered by vacuum fusion.

---

* It is not known if the combustion method for sulphur, which gives good accuracy in steel, is accurate for sulphur in molybdenum. This is now being determined.

TABLE 31. CHEMICAL ANALYSES OF MOLYBDENUM PURIFIED BY VACUUM ARC MELTING

Ingot Number	Number of Times ingot was Arc Melted	O_2	H_2	N_2	C	S	Ni	Mn	Cr	Al	Si	Cu	Fe
Melting Stock		(A)	(A)	(A)	0.001	0.015	0.005-0.05	0.001-0.01	0.001-0.01	<0.001	0.0005-0.005	0.0005-0.005	0.005-0.05
A7248A	1	0.0003	0.00016	0.0002	0.001	0.020	<0.005	<0.001	<0.001	<0.001	0.0005-0.005	0.0005-0.005	0.001-0.01
A7172B	2	0.0001	0.00021	0.0002	0.001	0.021	<0.005	<0.001	<0.001	<0.001	0.0005-0.005	0.0005-0.005	0.0005-0.005
A7251C	3	0.0002	0.00005	0.0002	0.002	0.023	<0.005	<0.001	<0.001	<0.001	0.0005-0.005	0.0005-0.005	0.001-0.01
A7250D	4	0.0004	0.00010	0.0003	0.001	0.024	<0.005	<0.001	<0.001	<0.001	0.0005-0.005	0.0005-0.005	0.0001-0.001
A7249E	5	0.0006	0.00011	0.0005	0.002	0.023	<0.005	<0.001	<0.001	<0.001	0.0005-0.005	0.0001-0.001	0.0005-0.005

Notes:

Oxygen, hydrogen, and nitrogen were analyzed by vacuum fusion. Accuracy of these analyses are believed to be: oxygen, ±0.001 per cent; hydrogen, ±0.00001 per cent; and nitrogen, ±0.0002 per cent.

Carbon and sulphur were analyzed by combustion methods. The accuracy of the carbon analyses is believed to be ±0.001 per cent. Sulphur was analyzed by a procedure known to have an accuracy on steels of ±0.005 per cent. Its accuracy on molybdenum is now being determined.

Nickel, manganese, chromium, aluminum, silicon, copper and iron were all analyzed by a spectrographic method whose accuracy is unknown. The concentrations shown here should be compared with each other rather than considered as absolute values.

(A) Oxygen, hydrogen, and nitrogen were not determined on this melting stock, but another lot of the same material contained 0.007 ± 0.001 per cent oxygen; 0.00031 ± 0.00005 per cent hydrogen; 0.001±0.001 per cent nitrogen; and 0.003 ± 0.001 per cent carbon.

Carbon content was not reduced, confirming results reported in the Seventh Report.

The maximum reduction of all impurities, other than carbon, was accomplished in three meltings, indicating that additional remelting is unnecessary.

The indicated increase in oxygen content, after the third melting, from 0.0001 to 0.0008 per cent is well above the analytical error, although contamination of the analytical samples is a possibility. If the ingots actually did pick up oxygen, no explanation is apparent at this time. This will require further investigation.

The hydrogen content of the ingots in Table 31 is higher than that of the ingots listed on page 333 of the Seventh Report, but is lower than that of the powder-metallurgy melting stock.

Table 31 shows that there was no contamination of the molybdenum by copper from melting in copper crucibles, or by iron from crushing ingots in a steel mortar for remelting.

It does not appear that additional purification can be accomplished with present techniques. It may be possible to increase purity somewhat by using vacuum arc-melted molybdenum for electrodes during the second and subsequent meltings.

Future Work

Nitrogen, sulphur, and certain metallic elements will be added in controlled quantities to high-purity molybdenum. Testing such ingots by the slow-bend test may permit the effect of these elements on ductility to be determined.

It is also planned to make a series of ingots adding small amounts of elements which should form stable oxides or nitrides in molybdenum if oxygen or nitrogen are present. Titanium, zirconium, boron, beryllium, and thorium will be tried.

(The data from which this report was prepared are recorded in B.M.I. Notebook No. 5850, pp. 92-93, inclusive.)

HIGH-PURITY MOLYBDENUM BY HALIDE DECOMPOSITION

(E. M. Sherwood and I. E. Campbell)

Introduction

This section of the report describes the preparation of high-purity molybdenum pentachloride for use in the deposition of high-purity molybdenum by the halide decomposition method.

Experimental Work

Description of Chloride Preparation System

Figure 55 illustrates schematically the functional arrangement of the apparatus used to prepare high-purity molybdenum pentachloride. Ordinary tank chlorine was led through a dibutyl phthalate bubbler to the first flask of the chlorine distillation unit. The distillation flasks were so arranged that a fairly large amount of solid chlorine could be collected by freezing by the expedient of placing a Dewar flask containing liquid air over the lower portion of the first chlorine flask. The chlorine was then transferred successively from flask to flask by shifting the liquid-air container. The solid chlorine was held for a time in the last chlorine flask and then permitted to vaporize slowly into the chlorinator. Figure 54 indicates the design of the chlorination unit. A discussion of this unit and the chloride collector will be given in the following section.

HIGH-PURITY MOLYBDENUM BY HALIDE DECOMPOSITION

(E. M. Sherwood and I. E. Campbell)

Introduction

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Nozzle cap

Asbestos wool

Nozzle —

Stainless steel tube

Constriction

Path of chloride

Crushed molybdenum

Asbestos cement

No. 14 gage chromel wire

Pyrex beads

Transite

A

Constriction

Gas outlet

Thermocouple tube

Chlorinator

Chloride Receiver

Thermocouple wires

Chlorine inlet

Thin glass partition

Molybdenum rod —"705" glass

Cobalt glass

Monel bellows

Molybdenum "hammer"

Note 1.   Material, pyrex glass unless otherwise specified

Note 2.   Stainless steel plates soft soldered to monel bellows

Scale: Approximately one-half size

Kovar ring — Stainless steel plate

Silver braze —

Arm for connection to deposition unit

FIGURE 54.   CHLORINATOR AND CHLORIDE RECEIVER

0-18819
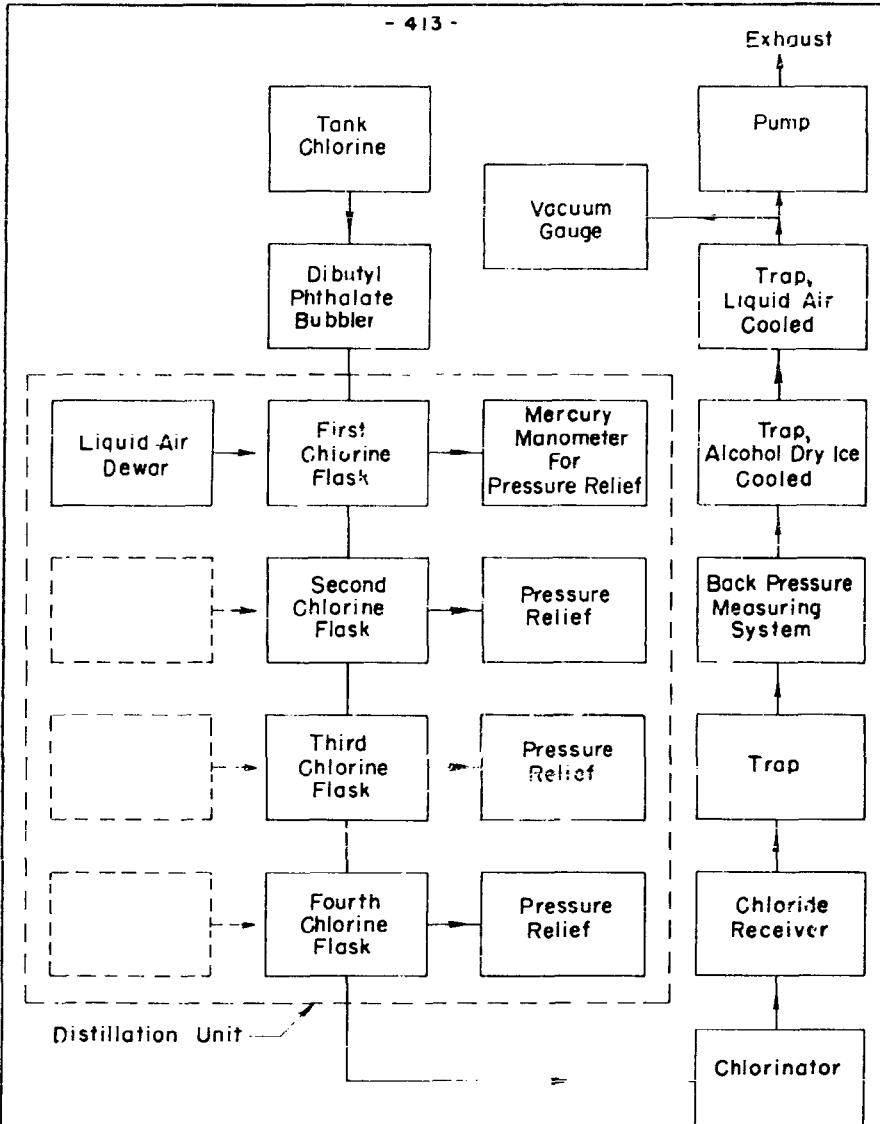
FIGURE 55. SCHEMATIC ARRANGEMENT OF CHLORINATION APPARATUS

O-18809

From the chlorinator and chloride collector, unused chlorine and other gaseous matter passed through a trap, a back-pressure measuring system, an alcohol-dry ice-cooled trap, a liquid-air-cooled trap, and thence to the vacuum pump and gauge. The latter was used to monitor the efficiency of pumping.

Pyrex glass was used throughout the system up to the trap following the chloride receiver. Although the remaining units were all Pyrex glass, connections between these units were made using vacuum hose and clamps with glyptol lacquer as a final sealant.

Chlorinator and Chloride Receiver

These units are depicted in Figure 54. The purified chlorine passed upward to the top of the nozzle cap, where it was constrained to flow downward in the annular space around the inlet tube and thence through the layer of Pyrex glass beads and again upward to the crushed molybdenum where chlorination took place. A small resistance furnace was used to heat the chlorinator. The chloride was driven out of the chlorinator and into the receiver by means of heat, the latter being furnished by a resistance wire-wound furnace and three conventional heat lamps, the latter mounted on flexible arms. Aluminum-foil reflectors were placed behind portions of the glass equipment in order to make more efficient use of the radiant heat. The heat lamps were found to be particularly effective in preventing stoppages of ring seal joints, in regions such as A in Figure 54, due to buildup of chloride.

Since the chloride has to be kept in a container sealed against the atmosphere, the design of the chloride receiver was somewhat special. First of all, a constriction was built into the piece of Pyrex glass

tubing which connected the chlorinator to the receiver. The outlet arm of the receiver was also constricted, so that sealing off could be accomplished with less difficulty. An arm for connecting the sealed-off chloride receiver to the deposition apparatus was also provided. The bottom wall of the receiver was made thin in the center and a hammer mechanism was provided for breaking the thin wall once the receiver was sealed to the deposition bulb. A Monel metal bellows, closed at one end by soldering in place a stainless steel plate carrying the molybdenum hammer, and joined at the other end to a Kovar sleeve, was provided. The Kovar sleeve was sealed into a Corning Type 705 glass ring which, in turn, was joined to the Pyrex support arm by means of a cobalt glass graded seal. Details of the receiver are also indicated in Figure 54.

Results

Several early runs were interrupted due to failures of one or two connections in the all-glass portion of the system.

The final run was successful. A fairly large amount of chlorine was collected in the solid state. It was found that alternate solidification and liquefaction cyclically repeated permitted a greater amount of chlorine to be collected for subsequent distillation. After distillation, chlorination at low pressure (less than 1 mm. of mercury) was begun. The chlorinator was maintained at a temperature of 860 ± 10°F. As the molybdenum pentachloride was formed, it sublimed into the collector and associated glass connections. A tendency for the exit arm to become plugged was noted. This could have been prevented by lengthening the arm in a vertical direction. It was also necessary to adjust the position of the heat lamps from time to time in order to maintain an

adequate rate of sublimation of the chloride. Some two weeks' continuous operating time was required in order to complete the chlorination at the low pressures employed.

The chloride receiver was sealed off from the remainder of the system to complete the operation.

Future Work

The deposition system will be set up and the chloride receiver attached. A generator of high-purity hydrogen (from titanium hydride) is nearly complete. Gas from this source will be used as a carrier in deposition by halide decomposition. It is hoped that a fairly large pure-molybdenum crystal bar can be prepared using this equipment.

ALLOYS OF MOLYBDENUM

(G. W. P. Rengstorff, H. B. Goodwin, and C. T. Greenidge)

INTRODUCTION

Rapid oxidation prevents utilization of the excellent high-temperature strength and ductility of molybdenum unless protective coatings are employed or unless the use of molybdenum is limited to non-oxidizing atmospheres. Because maintenance of protective coatings under stress is difficult, a program is under way to develop molybdenum alloys which will form and maintain their own protective coatings at elevated temperatures.

The alloy systems being investigated are listed in Table 32. The oxidation resistance of many of these alloys has been discussed in the Fifth, Sixth, and Seventh Quarterly Reports. At the beginning of this reporting period, thirty-eight alloys, marked with an asterisk in Table 32, remained to be made and tested for oxidation resistance. Gradient-composition ingots from these alloys have now been prepared and their oxidation resistance will be determined in the near future. This section of the report describes the preparation of these ingots.

EXPERIMENTAL WORK

To avoid making a very large number of ingots and yet completely cover the desired composition ranges, "gradient-composition" ingots are being used. Fortunately, the arc-melting process facilitates making such ingots. This is done by feeding charge material of gradually changing composition slowly into the water-cooled copper crucible during melting.

TABLE 32. MOLYBDENUM ALLOYS FOR A STUDY
OF OXIDATION RESISTANCE

Mo-Ni[(B)] (5, 6)[(A)]	Mo-Al (5)	Mo-Cr (5)
Mo-Ni-Al[(B)] (6, 7)	Mo-Al-Cr[(B)] (6)	Mo-Cr-Si (6)
Mo-Ni-Cr[(D)] (6, 7)	Mo-Al-Si[(E)]*	Mo-Cr-Ti*
Mo-Ni-Si (?)	Mo-Al-Ti[(C)] (6)	Mo-Cr-V*
Mo-Ni-Ti (7)	Mo-Al-V[(B)] (6)	Mo-Cr-Zr*
Mo-Ni-V (7)	Mo-Al-Zr[(B)] (6)	Mo-Cr-Co*
Mo-Ni-Zr (7)	Mo-Al-Co*	Mo-Cr-Fe*
Mo-Ni-Co (7)	Mo-Al-Fe*	Mo-Cr-W*
Mo-Ni-Fe (7)	Mo-Al-W*	
Mo-Ni-W (7)		
Mo-Si (6)	Mo-Ti (5)	Mo-V*
Mo-Si-Ti*	Mo-Ti-V*	Mo-V-Zr*
Mo-Si-V*	Mo-Ti-Zr*	Mo-V-Co*
Mo-Si-Zr(B) (6)	Mo-Ti-Co*	Mo-V-Fe*
Mo-Si-Co*	Mo-Ti-Fe*	Mo-V-W*
Mo-Si-Fe*	Mo-Ti-W*	
Mo-Si-W*		
Mo-Zr*	Mo-Co*	Mo-Fe*
Mo-Zr-Co*	Mo-Co-Fe*	Mo-Fe-W*
Mo-Zr-Fe*	Mo-Co-W*	
Mo-Zr-W*		
Mo-W*	Mo-B*	Mo-Sn*
	Mo-B-Fe*	

(A) The oxidation resistance is given in the quarterly reports, numbered
as shown in parenthesis. The Fifth Quarterly Report was dated
August 1, 1950, the Sixth was dated October 31, 1950, and the
Seventh was dated January 31, 1951.

(B) Two composition ranges were investigated for this alloy system.

(C) Three composition ranges were investigated for this alloy system.

(D) Five composition ranges were investigated for this alloy system.

(E) Ingots have been prepared for those alloy systems which do not have
a number in parentheses, but oxidation tests have not been made.

Since the ingot solidifies as formed, only the top layer being molten,
the result is an ingot which gradually changes in composition from bottom
to top. Usually the bottom of the ingot is pure molybdenum and the top
highly alloyed. The ingots were melted under argon* using a water-cooled,
molybdenum-tipped electrode.

Although no two alloying elements behaved exactly alike and the
same element sometimes acted differently in different ternary combinations,
some arc-melting characteristics were typical among the various alloy
series.

Aluminum typifies alloy additions which greatly lowered the
melting point of molybdenum, vaporized out of the melt, and rapidly
attacked the electrode. Aluminum additions always caused the arc to be
unstable, apparently because of large amounts of aluminum vapor coming
from the melt and because of rapid melting of the electrode. In fact, the
arc was so unstable that the crucibles were often burned out. The attack
of the electrode tip by aluminum vapor was so great that the tip sometimes
melted back to the water-cooled electrode before the end of the heat.
To minimize the attack on the electrode tip and also to reduce damage
resulting from instability of the arc, alloys containing aluminum were
melted with a comparatively low arc current. Also, the charge was fed as
rapidly as possible,so that the electrode would not be consumed before
the end of the heat. This procedure was possible because all the
aluminum-containing alloys had low melting points. Tin vaporized almost
as readily as aluminum when added to molybdenum.

---

* Argon of 99.92 per cent purity was normally used, but this gas was not
available for a time,so argon of 99.8 per cent purity was used for
some of the heats with no apparent harmful effects.

Other elements whose vapors attacked the electrode were boron, titanium, and occasionally chromium. Titanium- and chromium-containing alloys, unlike aluminum alloys, often had comparatively high melting points. Vaporization of titanium and chromium was considerably reduced by slow, rather than rapid, feeding of the melting stock. Apparently the vapor pressure of these elements was low if they dissolved immediately in a molten pool, rather than floated on the melt. Iron and cobalt often behaved similarly as far as vaporization was concerned. Although both vaporized readily, their vapors did not attack the electrode as did boron, titanium, and chromium vapors.

When direct current was used for melting, iron and cobalt were magnetically attracted to the electrode. The particles of these metals clung to the electrode and did not drop into the melt. The use of alternating current eliminated attraction of iron and cobalt to the electrode, but in argon, the charge was not melted, even though the current was sufficient to melt the electrode tip in less than one minute. Iron and cobalt were finally added successfully to molybdenum melts made with direct current by using commercial ferro-molybdenum containing 37 per cent iron* and by using a 50 per cent cobalt - 50 per cent molybdenum alloy. The latter was prepared at Battelle. Both alloys were only weakly magnetic and, therefore, were not attracted to the electrode. The use of ferro-molybdenum and the cobalt-molybdenum alloy resulted in less porous ingots than had been obtained previously, since these materials contained much less dissolved gas than did the electrolytic iron and the hydrogen-reduced cobalt rondelles first tried for introducing iron and cobalt into molybdenum.

---

* Ferro-chromium and ferro-aluminum were also used successfully.

Elimination of gases dissolved in the alloying agents, as well as in the powder-metallurgy molybdenum, was a constant problem. The most effective way of reducing porosity in ingots caused by gas was to melt slowly near the top of a 1-5/8-inch- or 2-inch-diameter mold. This procedure permitted gases to escape before the molten metal solidified. Even so, many of the ingots were rather porous, especially in the high-molybdenum end.

Alloys containing zirconium proved extremely difficult to melt with the usual arc currents of 900 amperes. A 1200-ampere direct current generator was borrowed and most of the zirconium alloys melted at 1200 amperes. Even at a current of 1200 amperes, melting was not quite so good as desired. At this current, the molybdenum electrode tips lasted for several hours. This was unexpected because, when melting pure molybdenum in argon, this same current melted the molybdenum electrode tips in a matter of minutes. The reasons for this difference in behavior of the molybdenum tips are not clear at the moment.

Additions of nickel, silicon, or vanadium did not usually cause difficulties in melting.

The melting time for preparing ingots weighing about 1-1/2 pounds varied from 15 to 90 minutes. The direct arc current varied from 700 to 1200 amperes.

On page 166 of the Fifth Quarterly Report is given a list of the metals used in preparing the alloys, their form, and their purity. Several changes and additions have been made since then. For that reason a new summary is given in Table 33 of this report.

A new type of melting crucible has been designed and put in use which permits quick replacement when burned out. This has expedited the

TABLE 33. METALS USED TO MAKE GRADIENT-COMPOSITION
MOLYBDENUM ALLOYS FOR OXIDATION TESTS

Metal	Physical Condition	Purity
Primary Molybdenum Feed	Powder pressed, then crushed to minus 6, plus 20 mesh. Not sintered.	Commercially pure, obtained from Fansteel Metallurgical Corporation. Contains approximately 0.005% carbon and probably about 0.01% or more oxygen.
Secondary Molybdenum Feed. Some ingots contain up to 20% of this feed.	Machined turnings.	Scrap from high-purity or commercially pure molybdenum.
Ditto	Crushed fines, minus 20 mesh.	The fines from crushed, commercially pure, sintered molybdenum.
Molybdenum Electrode Tips	5/8-inch-diameter rod, swaged, cleaned, and straightened.	Commercially pure, obtained from Westinghouse Electric Corporation. Probably contains about 0.003% carbon and 0.007% oxygen.
Aluminum	1/8-inch- (preferred) or 1/4-inch-diameter wire cut to 1/8- to 1/4-inch lengths.	99+% Aluminum
Aluminum-Iron	Crushed and sized to minus 6, plus 20 mesh.	Ingot A2089 contains 52.5% aluminum, 47.5% iron (nominal).
Boron	Granules, minus 6 mesh.	97+% boron, obtained from Cooper Metallurgical Association.
Boron-Iron	Crushed and sized to minus 6, plus 20 mesh.	Battelle Lot 383. Vendor's analysis: 17.97% boron, 0.44% silicon, 0.10% aluminum, 0.37% carbon.

TABLE 33. (Continue')

Metal	Physical Condition	Purity
Cobalt (used successfully in Mo-Co-Ni alloys only)	Rondelles crushed and sized to minus 6, plus 20 mesh.	Battelle Lot 599. Battelle anal·ـۃs: 99.4% cobalt, 0 ـۅ% carbon, 0.45% nitrogen, 0.10% iron. Known to contain considerable amounts of hydrogen.
Cobalt-Molybdenum	Crushed and sized to minus 6, plus 20 mesh.	Ingot A7264. Vacuum induction melted. Nominal 50% cobalt, 50% molybdenum.
Chromium	Crushed and sized to minus 6, plus 20 mesh.	Fused chromium. Battelle Lot 594. Battelle analysis: 0.02% carbon, 0.31% silicon, 0.27% iron, 0.3% aluminum, 0.041% nitrogen, < 0.01% sulphur.
Chromium-Iron	Crushed and sized to minus 6, plus 20 mesh.	Ingot A4698. Vacuum induction melted. Battelle analysis: 59.8% chromium, 25.3% iron, 14.9% molybdenum, 0.02% carbon.
Iron (used successfully in Mo-Fe-Ni alloy only)	Electrolytic iron flakes crushed and sized to minus 6, plus 20 mesh.	Battelle Lot 606. Battelle analysis: 0.005% phosphorus, 0.004% sulphur, 0.001% nitrogen. Known to contain considerable amounts of hydrogen.
Iron-Molybdenum	Crushed and sized to minus 6, plus 20 mesh.	Battelle Lot 574. Vendor's analysis: 62.8% molybdenum, 0.45% silicon, 0.05% carbon.
Iron-Aluminum	Given under "Aluminum-Iron".	
Iron-Chromium-Molybdenum	Given under "Chromium-Iron-Molybdenum".	

TABLE 33. (Continued)

Metal	Physical Condition	Purity
Nickel	Shot, about 1/8 to 3/16 inch in diameter.	Baker's analyzed, low cobalt. Baker's analysis: 0.001% copper, 0.03% iron, 0.000% lead, 0.00% zinc, 0.00% cobalt.
Silicon	Crushed and sized to minus 6, plus 20 mesh.	Fused silicon. Battelle Lot 553. Battelle analysis: 96.8% silicon, 1.0% iron.
Tin	20 mesh.	Baker's C. P. Vendor's analysis: 0.00008% arsenic, 0.0008% copper, 0.003% iron, 0.001% lead, 0.0009% zinc.
Titanium	Sponge crushed to and sized to minus 1/4 inch, plus 8 mesh.	DuPont Process A sponge. Ductile titanium. Purity not known.
Vanadium	Granules, generally minus 6 mesh with few fines.	Battelle analysis: 90.56% vanadium. Typical analysis furnished by vendor: 1.0% aluminum, 0.9% silicon, 2.05% iron, 0.1% carbon, 0.08% sulphur, 0.02% phosphorus, 0.04% magnesium. Much of the remainder is oxygen and nitrogen.
Tungsten	Scrap pieces crushed and sized to minus 6, plus 20 mesh, but minus 20 mesh was preferred and used for most alloys.	Commercially pure tungsten scrap.
Zirconium	Sponge crushed and sized to minus 6, plus 20 mesh.	Bureau of Mines sponge.

work with alloys which cause unstable arcs and frequent crucible burn-outs.

FUTURE WORK

In the immediate future, oxidation tests will be made on the alloys discussed in this report. An evaluation of all of the alloys so far prepared will then be made. This will complete the first phase of the work on development of oxidation-resistant alloys.

The direction of further work will be decided after the evaluation of the past results. Tentative plans are to investigate the oxidation resistance of the more promising alloys more thoroughly and to determine their mechanical properties.

Further work on ternary or perhaps on quaternary alloys may be indicated. Also the more expensive alloys, such as platinum, tantalum, and columbium, should be considered. No attempt has been made to prepare alloys of molybdenum with manganese, lithium, or bismuth because of the volatility of these elements at the melting point of molybdenum. Powder-metallurgy methods may be resorted to for the preparation of a few alloys of this type.

If certain of the alloys are oxidation resistant, but are too brittle to use as the major component of structures, they may, nevertheless serve as protective coatings when applied in the same manner as molybdenum silicide. Also, it may be possible to electroplate successive layers of alloys on molybdenum so that, under oxidizing conditions, the desired oxide film is formed.

Pretreatments to form the desired initial scale have been investigated only to a limited extent. Treatments in controlled atmospheres should be considered. Also, an acid dip treatment[1], such as is used for improving the oxidation resistance of tungsten, should be investigated.

(Data from which this report is written were taken from B.M.I. Laboratory Record Books Nos. 5850, pp. 18-100, and 6112, pp. 1-2, inclusive.)

(1) Bueckle, H., "Surface Protection of High-Melting Metals to Increase Their Resistance to Scaling", Metallforschung, V. 1, pp. 81-86 (1946); abstracted in Metal Progress, V. 59, pp. 288-290 (1951).

HIGH-TEMPERATURE-PROPERTY MEASUREMENT

(J. A. VanEcho, A. B. Westerman, and H. C. Cross)

INTRODUCTION

Creep-rupture tests were conducted on Westinghouse powder-metallurgy molybdenum in the as-received condition at 1600, 1800, and 2000°F. Several tests were conducted on Fansteel powder-metallurgy and Climax arc-cast molybdenum at 1600, 1800, and 2000°F. to complete the series previously started on these materials.

Creep-rupture tests at 1800°F. in a hydrogen atmosphere are now being run on recrystallized arc-cast molybdenum.

Arc-cast molybdenum bar stock, supposedly representing two different grain sizes, has been received from the Climax Molybdenum Company for testing. Recrystallization characteristics of this material are now being determined. Powder-metallurgy molybdenum sheet for a study of the effect of preferred grain orientation on rupture properties at 1600°F. is being supplied by the Fansteel Metallurgical Corporation. This material has also been received.

EXPERIMENTAL WORK

Equipment

An additional vacuum creep furnace is being constructed for operation at temperatures as high as 2000°F. There has been some delay in the construction of this furnace because of difficulty in obtaining the necessary parts. When completed, this furnace will make a total of six

vacuum units available for conducting tests in vacuum. However, due to
space shortage, only three creep units were in operation during the past
quarter.

Creep-Rupture Results

All of the creep-rupture data obtained to date on molybdenum are
shown in Figure 56. Included in this figure are the data obtained during
the past quarter on Westinghouse powder-metallurgy molybdenum; these
data are listed in Table 34. Table 35 contains the results of several
rupture tests conducted on Fansteel powder-metallurgy and Climax arc-cast
molybdenum at 1600, 1800, and 2000°F. Table 36 and Figure 57 show the
creep-rupture data obtained on recrystallized arc-cast molybdenum as
tested in vacuum and in a dry-hydrogen atmosphere. Table 37 shows the
weight changes occurring in powder-metallurgy molybdenum during regular
creep-rupture testing in vacuum.

Creep-Rupture Testing in Vacuum

As shown in Figure 56, the Westinghouse powder-metallurgy
molybdenum in the as-received condition had an intermediate creep-rupture
strength at 1600, 1800, and 2000°F. when compared with all of the other
types of molybdenum tested. Examination of the microstructure after test
showed partial recrystallization of the molybdenum at 1600 and 1800°F.
At 2000°F., recrystallization was complete after only a short time in test.

Results of tests on stress-relieved (1800°F. for 1 hour)
Westinghouse powder-metallurgy molybdenum were presented in the last
quarterly report, but are shown here again (Table 34) for comparison with
the data on the as-received material. As shown in Figure 56, there was
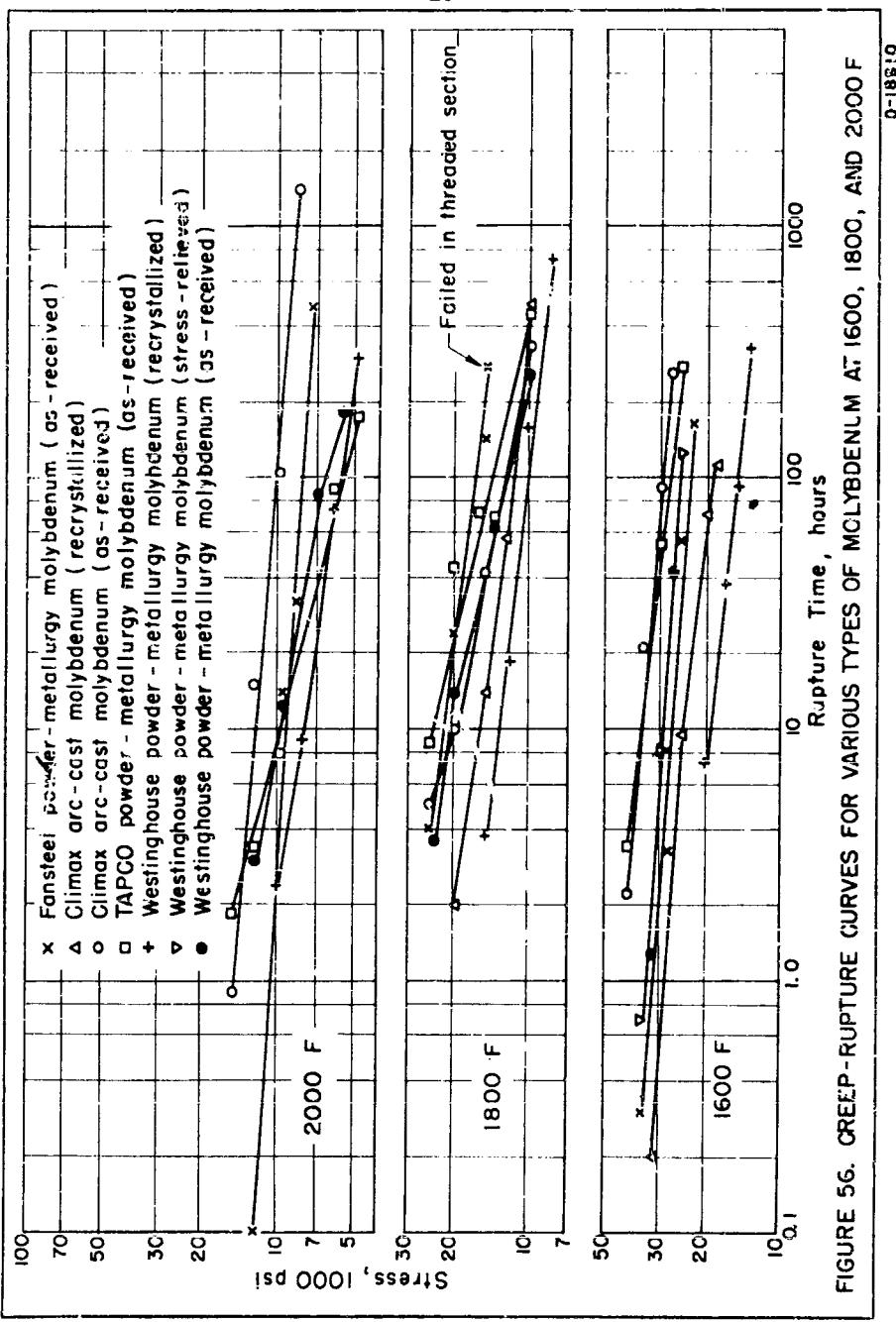
FIGURE 56. CREEP-RUPTURE CURVES FOR VARIOUS TYPES OF MOLYBDENUM AT 1600, 1800, AND 2000 F

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TABLE 34. CREEP-RUPTURE DATA OBTAINED ON
WESTINGHOUSE POWDER-METALLURGY
MOLYBDENUM AT 1600, 1800,
AND 2000°F.

Stress, p.s.i.	Rupture Time, Hours	Elongation, Per Cent	Reduction of Area, Per Cent	Microstructure	
				Before Test	After Test
			1600°F.		
32,500*	1.3	24.0	92.8	C. W.	P. R.
27,500*	42.7	23.8	94.7	C. W.	P. R.
35,000	0.7	24.4	93.4	S. R.	P. R.
30,000	8.1	23.0	93.2	S. R.	P. R.
25,000	125.0	22.0	89.5	S. R.	P. R.
			1800°F.		
24,000*	3.6	23.8	95.1	C. W.	P. R.
20,000*	14.0	27.0	94.5	C. W.	P. R.
14,000*	63.5	30.6	91.9	C. W.	P. R.
10,000*	259.3	35.0	41.0	C. W.	P. R.
			2000°F.		
12,500*	3.0	29.0	30.7	C. W.	R
9,500*	12.2	12.9	14.7	C. W.	R
7,000*	86.7	8.9	7.8	C. W.	R
5,500*	184.1	4.8	2.7	C. W.	R

C. W. -- Cold worked.
P. R. -- Partially recrystallized.
R   -- Recrystallized.
S. R. -- Stress relieved (1 hour at 1800°F.).
*   -- Tests conducted during the past quarter.

TABLE 35. CREEP-RUPTURE DATA OBTAINED ON FANSTEEL
POWDER-METALLURGY AND CLIMAX ARC-
CAST MOLYBDENUM

Stress, p.s.i.	Rupture Time, Hours	Elongation, Per Cent	Reduction of Area, Per Cent	Microstructure Before Test	After Test
1600°F. - Climax Arc-Cast Molybdenum					
27,500	261.3	17.9	85.5	C. W.	P. R.
1800°F. - Fansteel Powder-Metallurgy Molybdenum					
25,000	4.0	31.2	88.4	C. W.	---
15,000	144.2	13.6	53.8	C. W.	---
2000°F. - Fansteel Powder-Metallurgy Molybdenum					
7,500	478.1	1.9	1.2	C. W.	---

C. W. — Cold worked.
P. R. — Partially recrystallized.

TABLE 36. CREEP-RUPTURE DATA OBTAINED ON CLIMAX
ARC-CAST MOLYBDENUM AT 1800°F.
TESTED IN VACUUM AND IN
DRY HYDROGEN

Stress, p.s.i.	Rupture Time, Hours	Elongation, Per Cent	Reduction of Area, Per Cent	Microstructure	
				Before Test	After Test
In Vacuum					
20,000	2.0	70.3	85.3	R	R
15,000	14.0	41.3	81.1	R	R
12,500	57.7	40.6	80.6	R	R
10,000	481.9	17.4	48.9	R	R
In Dry Hydrogen					
20,000*	1.3	54.2	87.1	R	R
15,000*	11.2	72.1	93.4	R	R
12,500*	34.4	62.9	92.9	R	R
10,000*	146.8	79.6	91.4	R	R

R -- Recrystallized.
* -- Tests conducted during the past quarter.
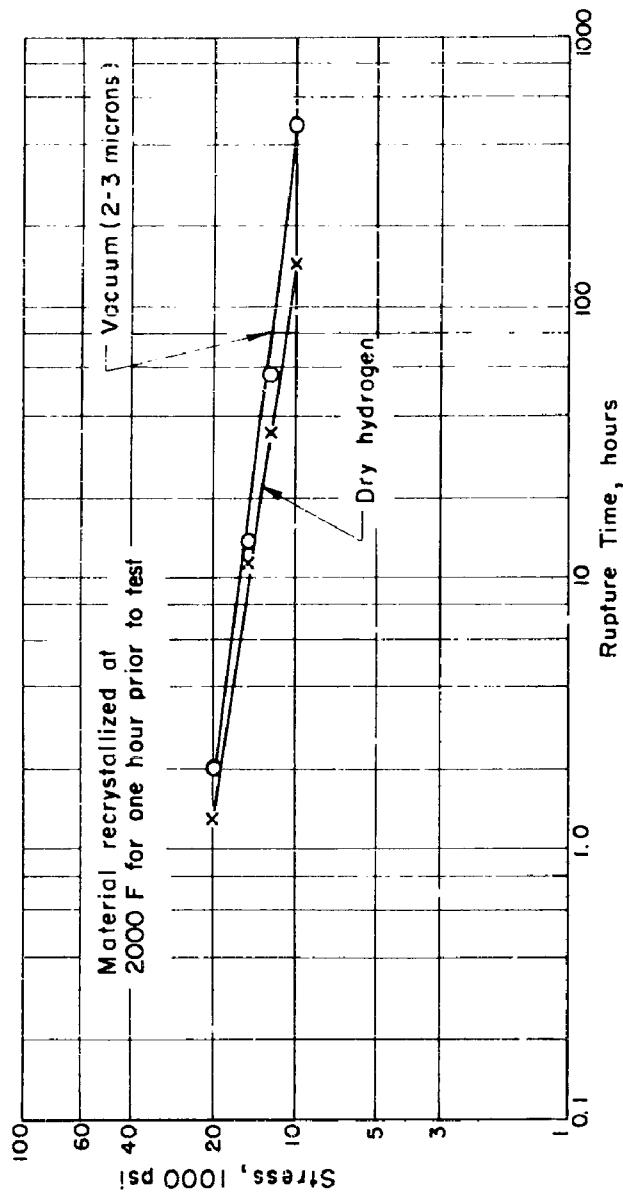
FIGURE 57. EFFECT OF AMBIENT ATMOSPHERE ON CREEP-RUPTURE PROPERTIES OF RECRYSTALLIZED ARC-CAST MOLYBDENUM AT 1800 F

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TABLE 37. DETERIORATION OF TAPCO AND WESTINGHOUSE
POWDER-METALLURGY MOLYBDENUM SPECIMENS
DURING RUPTURE TESTING IN VACUUM AT
1600 TO 2000°F.

Specimen Number(1)	Temperature of Test, °F.	Rupture Time, Hours	Change in Weight*	
			% Gain	% Loss
T7	1600	53.2	--	.0520
T9	1600	276.3	--	.0030
T4	1800	8.9	.0038	--
T5	1800	44.0	.0003	--
T12	1800	69.4	--	.0031
T10	1800	73.0	--	.0211
T13	1800	452.3	--	.0147
T8	2000	90.2	--	.0369
T11	2000	175.5	--	.0006
W11	1600	93.6	--	.0146
W14	1600	327.7	--	.0000
W6	2000	2.4	--	.0873
W10	2000	9.2	--	.0562
W12	2000	301.0	--	.0350

(1) T -- Thompson Products powder-metallurgy molybdenum.
     W -- Westinghouse powder-metallurgy molybdenum.
*   -- Accuracy of weighing balance -- about ± .002%.

no difference in the 1600°F. creep-rupture strengths of this material in these two conditions. Rupture-test results on the as-received powder-metallurgy molybdenum at this temperature fell on the curve of results for the same material in the stress-relieved condition. This comparison cannot be made at 1800 and 2000°F., since tests on the stress-relieved material were made only at 1600°F.

Such close similarity in creep-rupture strength at 1600°F. of the Westinghouse powder-metallurgy molybdenum, as shown in Figure 56, in the stress-relieved (1 hour at 1800°F.) and as-received (swaged) conditions was questionable. As a result, X-ray diffraction patterns were made on these two materials and also on the recrystallized (1 hour at 2200°F.) molybdenum to determine the degree of stress relief in the stress-relieved material as compared with the other two materials.

The recrystallized sample showed spotted diffraction lines, as expected, of a coarse-grained material. The other two materials (swaged and stress-relieved) showed sharp continuous diffraction lines that were similar for both materials. This seemed to indicate that the swaged (as-received) material was relatively free from stresses and, therefore, possibly also stress relieved after the swaging operation.

To verify these results, a sample of the powder-metallurgy molybdenum was intentionally cold worked by grinding and then annealed for 1 hour at 1800°F. X-ray diffraction patterns on both of these materials appeared as expected. The cold-worked material showed broad diffraction lines, while the annealed material showed lines similar to those of the swaged and stress-relieved material, thus verifying the original results.

The data in Table 34 on the as-received (cold-worked) Westinghouse powder-metallurgy molybdenum generally showed a decrease in ductility at 2000°F. as compared with the ductility at 1600 and 1800°F. There is also a sudden decrease in ductility at 2000°F. as the time of test at temperature increased. It is shown in Table 34 that a small increase in time at 2000°F., from 3.0 to 12.2 hours, results in about a 50 per cent decrease in elongation and reduction of area. This rapid decrease in ductility at 2000°F. also occurred in TAPCO and Fansteel powder-metallurgy and Climax arc-cast molybdenum. Possibly the molybdenum specimens pick up oxygen at 2000°F., even though the tests are conducted in a vacuum of about 2-3 microns pressure, and consequently, lose ductility.

Tests are now being conducted in a hydrogen atmosphere at 1800°F. and a few may also be run at 2000°F. The results of these tests should show whether the increase in brittleness with increasing time at 2000°F. is inherent in molybdenum or is caused by an insufficient vacuum in the testing furnace. The creep-rupture testing carried out to date in a hydrogen atmosphere will be discussed in a later section.

While awaiting the receipt of more test material, some additional creep-rupture tests were conducted on Fansteel powder-metallurgy and Climax arc-cast molybdenum in the as-received condition at 1600, 1800, and 2000°F. These were run for the purpose of completing the series of tests started previously on as-received material. The results are also shown in Figure 56 and Table 35.

One test was conducted at 1600°F. on Climax arc-cast material, two tests at 1800°F. on Fansteel powder-metallurgy molybdenum, and c test at 2000°F., also on the Fansteel molybdenum. All tests fell in line with the established curve for each material, as shown in Figure 56. Except for extending the curve in each case, there was no change indicated in the relative strengths of these materials.

With the completion of these tests, the phase of the program concerned with determining the creep-rupture strength of commercially available molybdenum is concluded. The relative merits of each material have already been discussed in this and previous reports, and no further mention of them will be made at this time. The complete set of creep-rupture results on all of the materials tested at 1600, 1800, and 2000°F. are illustrated in Figure 56.

Creep-Rupture Testing in Hydrogen

The modified over-all program, as presented in the Seventh Quarterly Report, included determining the effect of ambient atmosphere, particularly hydrogen, on the creep-rupture properties of arc-cast molybdenum. This part of the program has been started and preliminary results are shown in Table 36 and Figure 57.

The large vacuum furnace on loan from the Bureau of Ordnance, U. S. Navy, is being used for conducting these tests in a dry-hydrogen atmosphere. Oxygen and moisture are removed from the hydrogen by passing the gas through Drierite, soda lime, platinized asbestos, activated alumina, and phosphoric acid anhydride, in that order.

Because of a much greater heat loss by convection and conduction, approximately 200 per cent more input power is required to run the tests

in hydrogen than in vacuum at temperatures of 1600 to 2000°F. Therefore, all tests conducted in gaseous atmosphere at 1600 F. or higher will be conducted in the large unit, since the power available to the small furnaces is inadequate.

Table 36 and Figure 57 show the results of tests conducted on recrystallized arc-cast molybdenum at 1800°F. in a dry-hydrogen atmosphere. For comparison, similar creep-rupture data obtained previously on the same material tested in a vacuum of 2-3 microns pressure are also shown.

On the basis of these limited data, at 1800°F. this material tested in dry hydrogen showed slightly lower rupture strength and higher ductility than when tested in vacuum. The slightly steeper slope of the creep-rupture curve for tests in hydrogen also indicated a greater rate of decrease in creep-rupture strength as the test time increased. This reduction in creep strength and corresponding increase in ductility is probably the result of a lower oxygen content of the material tested in hydrogen as compared with testing in vacuum. The conclusion, therefore, would seem to be that the samples tested in vacuum pick up more oxygen than those tested in hydrogen. This observed effect resulting from testing in a hydrogen atmosphere should be verified by similar tests on other types of molybdenum. Analyses are being made to determine the oxygen and carbon contents of each specimen tested in hydrogen and in vacuum before and after test, and any changes will be noted. These results are not yet available, but will be presented in a subsequent report.

Deterioration of Creep-Rupture
Specimens During Test

A few of the regular creep-rupture specimens were weighed before and after test in vacuum in order to determine the extent of loss or gain in weight due to oxidation. It could then be determined from these data whether there was a gradual change in the stress imposed on the material as a result of changes in the dimensions of the specimens during test. The weight measurements were made on TAPCO and Westinghouse powder-metallurgy molybdenum tested in vacuum at 1600, 1800, and 2000°F. The measurements are shown in Table 37.

The greatest change of weight, 0.0873 per cent loss, occurred in Specimen W6 tested at 2000°F. Even with this maximum loss in weight, however, the effect on the stress can be considered as negligible; the experimental error in measuring a specimen and calculating the load will seldom permit a closer tolerance.

FUTURE WORK

Of immediate concern is the continued determination of the effect of a hydrogen atmosphere on the creep-rupture properties of arc-cast molybdenum. Beyond this, the program as outlined in the Seventh Quarterly Report will be followed:

(1) To determine the rupture properties of molybdenum bars with coarse and fine recrystallized grain sizes as obtained from two different sizes of ingot. The preliminary work of recrystallizing this material to get the maximum difference in grain size is now being done. Creep-rupture

tests will then be made on materials of the two grain sizes at 1800 and 2000°F.

(2) To determine the effect of preferred orientation on the properties of molybdenum sheet. This material has been received from the Fansteel Metallurgical Corporation and tests will be started immediately at 1600°F.

(3) To determine the effect of impurities on the properties of molybdenum, for example, the effect of carbon, oxygen, nitrogen, and perhaps other elements normally present in commercial molybdenum.

(4) To determine the rupture properties of arc-cast molybdenum in the as-cast condition, for comparison with the properties of wrought arc-cast material.

(5) To determine the effect of certain processing variables, such as amount and temperature of hot working.

(The data from which this report was prepared are recorded in B.M.I. Record Books Nos. 4965, pp. 95-100, and 5250, pp. 55-75.)

THE IMPROVEMENT OF ROOM-TEMPERATURE
MECHANICAL PROPERTIES OF MOLYBDENUM

(W. E. Few and G. K. Manning)

THE Mo-C AND Mo-O SYSTEMS

Introduction

During the reporting period of November 1, 1950, to January 31,
1951, attempts were made to determine the limit of solubility of oxygen
in molybdenum by passing oxygen over the surface of molybdenum wire at
such a pressure that a thin coating of MoO_2 was maintained on the wire
surface. After sufficient time to assure uniform dissolved-oxygen
content within the wire, the wire was to be rapidly cooled to room
temperature and the oxide coating removed from the surface by mechanical
methods. Vacuum-fusion analysis of the wire would then indicate the limit
of solubility for that particular temperature. However, it became
evident that this procedure could not be used when it was found that
disconnected intergranular films of oxide formed well below the wire
surface at the same time a surface film was established. Such internal
oxide particles would invalidate the equivalence between total oxygen,
as given by vacuum-fusion analysis, and the saturation value. During this
reporting period (February 1, 1951, to April 30, 1951), the major portion
of the effort was placed on the study of the ductility of wrought
molybdenum.

Experimental Work

A number of tests concerning the Mo-O system were made, however, in which the furnace was charged with a particular amount of oxygen before starting the heat treatment. The heat treatment was carried out in a closed system, as contrasted to the flowing atmosphere used previously. It was hoped that, by choosing an appropriate initial oxygen pressure for each temperature, an oxygen film would form on the surface of the wire and remain for sufficient time to permit the dissolved oxygen within the metallic molybdanum to reach equilibrium. Eventually, this surface oxide film would disappear because of the volatility of MoO_2 and the gradual depletion of oxygen within the closed system. If the internal oxide films disappeared at the same time the surface oxide film disappeared, then by stopping the treatment at the moment the surface film disappeared and analyzing the remaining metallic molybdenum for oxygen, the solubility limit of oxygen could be determined.

It developed that this procedure was no more successful than the first approach to the problem. An oxide film was formed on the wire surface, as expected, but this film would not persist sufficiently long to give assurance that equilibrium had been established within the interior of the wire. At 2500°F. with an initial pressure of 2 mm. Hg of oxygen, the film disappeared in 5 minutes, as evidenced by the emissivity change of the wire surface. At higher temperatures, the oxide film disappeared in even less time.

In addition to this, it was found that, in a closed system initially charged with oxygen, the pressure dropped rapidly in the first two or three minutes, then gradually increased until it eventually

exceeded the initial pressure. One analysis of the gas in the furnace after heating the wire for 30 minutes at 2500°F. showed it to consist of 60 per cent CO, 25 per cent H_2, and 15 per cent N_2. The source of the gas probably was a combination of adsorbed gas on the furnace wall, high temperature leaks in the furnace shell, dissolved gas in the molybdenum wire, and perhaps decomposition of the rubber seals used in the furnace shell. The build-up in pressure showed, however, that it would be quite difficult to maintain an atmosphere of constant composition in the furnace when operating it as a closed system.

Present plans are to again employ a flowing atmosphere in the furnace. The furnace will be evacuated and the wire heated to the desired temperature. With the vacuum pump still operating, oxygen will be bled into the furnace by means of two needle valves in series. By slowly increasing the oxygen pressure, the point will be reached at which an oxide film appears on the wire surface. This film will be removed and the cycle repeated using an oxygen pressure just below that which leads to a film formation. If metallographic examination indicates that such wire samples contain no internal oxide phase, they will be analyzed for oxygen. The results should be indicative of the limit of solubility of oxygen in molybdenum.

The 0.080-inch-diameter molybdenum wires used in attempting to establish an experimental procedure were found to be extremely ductile when finally removed from the furnace. They would stand innumerable reverse bends and exhibited 40 per cent elongation and 50 per cent reduction of area in a tensile test. In addition, they were very easy to polish metallographically by either mechanical or electrolytic means.

The wires had been heated several times with the furnace initially
charged with oxygen and then subsequently heated several times in a
vacuum of a few microns of Hg. Presumably, the oxidizing treatment
served to eliminate all carbon from the wire and the vacuum treatments
reduced the oxygen, nitrogen, and hydrogen contents to low values. This
suggests a means of producing molybdenum of "super high purity" on a
laboratory scale.

STUDY OF THE EFFECT OF CARBON
ON THE DUCTILITY OF WROUGHT MOLYBDENUM

(W. E. Few and O. K. Manning)

Introduction

The heat-treating experiments causing embrittlement of
commercial wrought molybdenum wire have been continued. The first
systematic program set up to study this effect has been completed.

Both room-temperature bend tests and tensile tests have been
used in these investigations. The results of these tests indicate the
variable causing this effect may not be carbon. However, what solute
element it may be cannot be determined from the experimental data
currently available. The actual transition from a ductile to brittle
material starts to occur when the wire is quenched from 3600°F.

It has also been found that this material (18-gauge molybdenum
wire) is susceptible to quench aging at room temperature if it is
quenched from 3800°F. How wide a temperature range the wire can be
quenched from and cause room-temperature aging is not known at the present
time. However, it has been found that overaging the wire at 2500°F. to
3500°F., after quenching from 3800°F., produces a relatively ductile
equiaxed molybdenum.

Ultimately it must be learned what impurity or impurities are
responsible for the effects observed. Also, the form and distribution in
which they occur must be determined.

Experimental Work

The experiments on the first program set up to evaluate the
effect of carbon on the ductility of wrought molybdenum, both as a solute
element and precipitated carbide, have been completed. (The detailed
program was presented and discussed in the Seventh Quarterly Report.)
Briefly, it entailed numerous heat treatments of 18-gauge molybdenum wire
and two different carbon contents. Wires containing 0.002 per cent C
and 0.011 per cent C were given identical heat treatments and then
subjected to the same tests. Both the Olsen stiffness test (bend test)
and a tensile test were used to determine the effects of heat treatment.

All samples were heated to 3800°F. for 15 minutes (in an
atmosphere of purified argon) and quenched. Some were held at temperature
for 1 hour. The 15-minute heat treatment supplied samples, all of the
same grain size. They were then given a reheating treatment at
temperatures from 2000°F. to 3800°F. for 15 minutes and quenched. One
group of samples was not given the initial 3800°F. heat treatment.
Instead, these samples were heated directly to the various temperatures
used for the reheating treatment between 2000°F. and 3800°F.

This more detailed program confirmed the results of the
exploratory experiments of the same type discussed in the Sixth Quarterly
Report. They indicated the room-temperature ductility of wrought
molybdenum could be altered by a simple series of heat treatments. Wires
quenched from 3800°F. were brittle, but if the same material was reheated
to temperatures between 2500°F. and 3500°F., it was found to be quite
ductile in terms of the bend test and tensile test.

Figure 58 to Figure 63 shows graphs of the results from the
bend tests and tensile tests on both the 0.002 per cent C and 0.011 per
cent C materials. The per cent elongation snown in the tensile-data
graphs was determined by recording the loads and amount of elongation,
for a given load, taken with sharp-pointed dividers at any particular time
during the test. After rupture, the total elongation was measured by
placing the two halves of the fractured specimen together and measuring
the amount of increase within the initial 2-inch gauge marks. Since this
method of determining elongation is not influenced by slip in the grips,
the dip present in some of the curves is probably due to a non-homo-
geneous yield. This same effect has been observed in other metals, but
an explanation of the mechanism causing such an effect is not known.
The initial strain rate used in all tensile tests was = 0.0005 sec.$^{-1}$.
For simplification of graphs and ease of reading, all available data
have not been plotted on these graphs. Only plots necessary to indicate
the effects of these heat treatments have been used. However, data on
all samples are presented in Tables 38 and 39.

The results are similar for both types of material investigated,
i.e., 0.002 per cent C and 0.011 per cent C wire. Also, the transition
from ductile to brittle behavior occurs in both materials when they are
quenched from about 3600°F., but is more pronounced when they are quenched
from 3800°F. All the carbon in the lower carbon wire containing 0.002 per
cent C should be in solution at temperatures above about 2100°F. If
dissolved carbon were the cause of the embrittling, then the embrittlement
should be associated with this temperature or some lower temperature. In
the higher carbon wire, all the carbon should be in solution at a tempera-
ture of about 3400°F. The data indicate that both wires are embrittled to
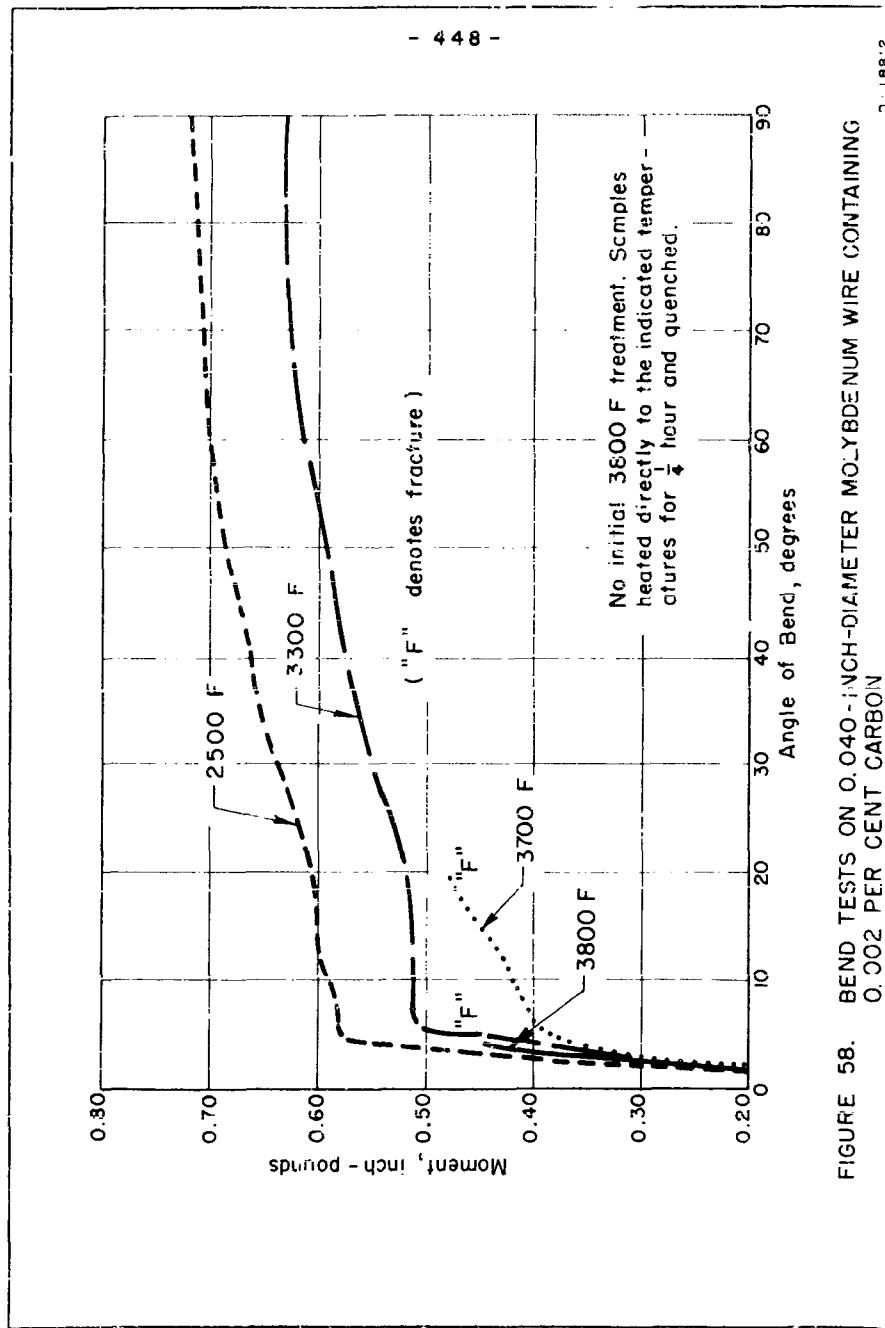
FIGURE 58. BEND TESTS ON 0.040-INCH-DIAMETER MOLYBDENUM WIRE CONTAINING 0.002 PER CENT CARBON

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FIGURE 59. TENSILE TESTS ON 0.040-INCH-DIAMETER MOLYBDENUM WIRE CONTAINING 0.002 PER CENT CARBON
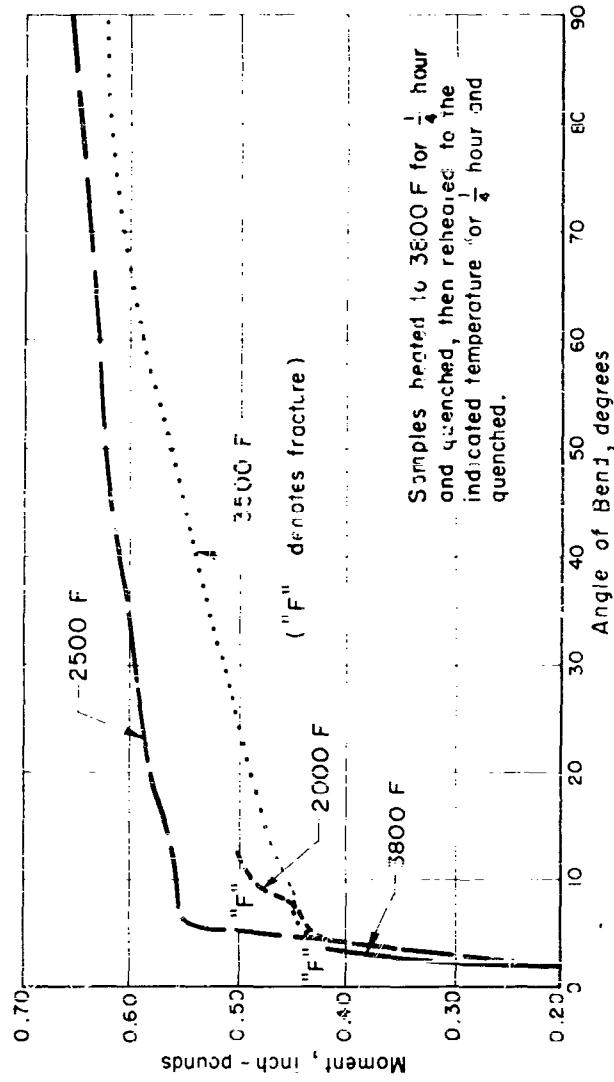
FIGURE 60. BEND TESTS ON C.040 - INCH - DIAMETER MOLYBDENUM WIRE
CONTAINING 0.002 PER CENT CARBON

Sample heated to 3800 F for $\frac{1}{4}$ hour and quenched, then reheated to the indicated temperatures for $\frac{1}{4}$ hour and quenched.

3500 F

2500 F

2000 F

3800 F

Stress, 1000 psi

75
70
65
60
55
50
45
40
35
30
25

Elongation in 2 inches, per cent

5   IC   15   20   25   30   35   40
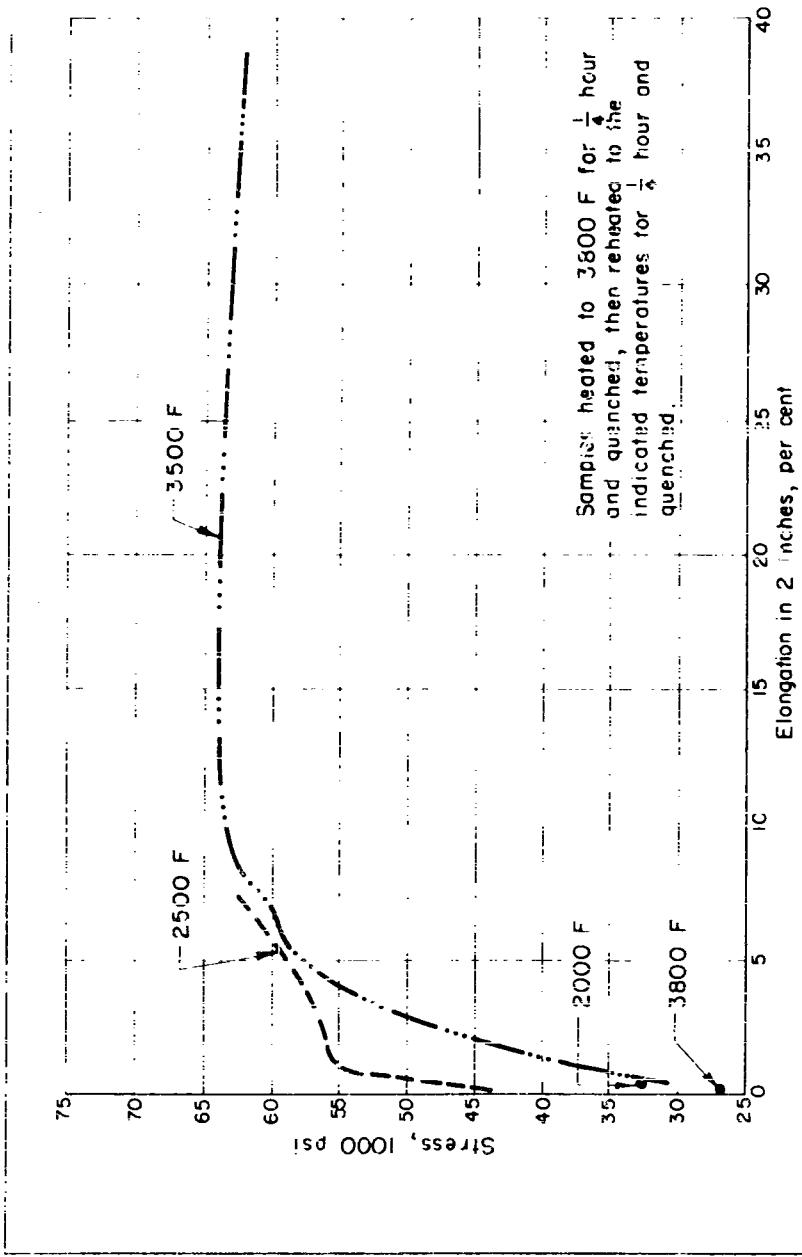
FIGURE 61. TENSILE TESTS ON 0.040-INCH-DIAMETER MOLYBDENUM WIRE CONTAINING 0.002 PER CENT CARBON

0-18815
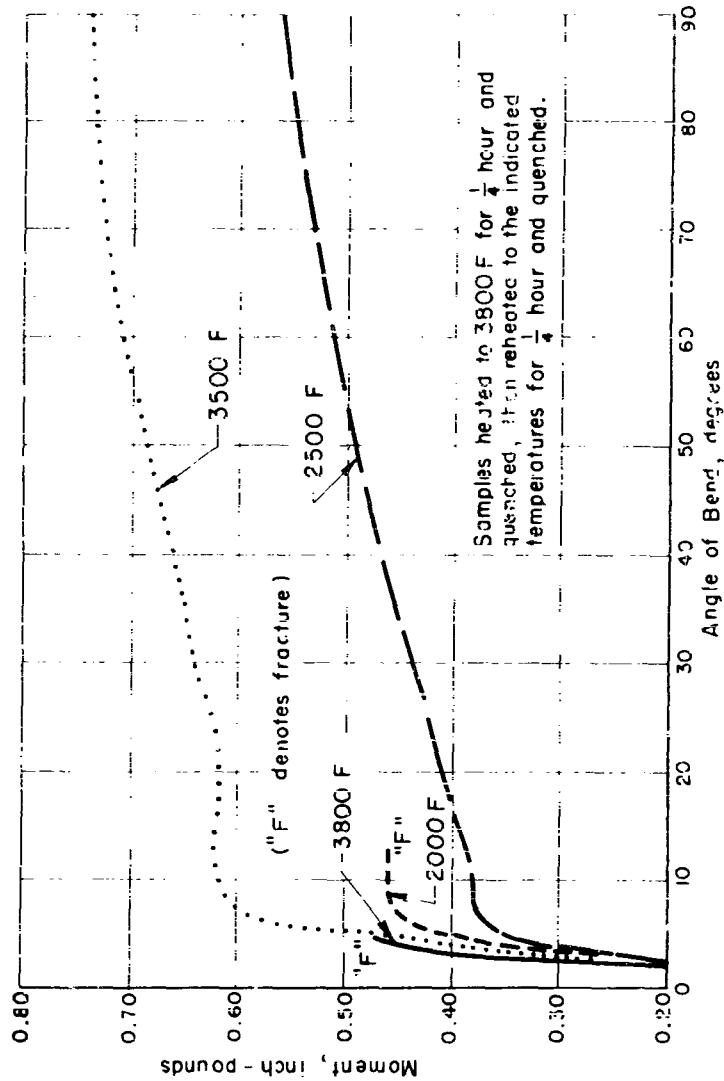
FIGURE 62. BEND TESTS ON 0.040-INCH-DIAMETER MOLYBDENUM WIRE CONTAINING 0.011 PER CENT CARBON
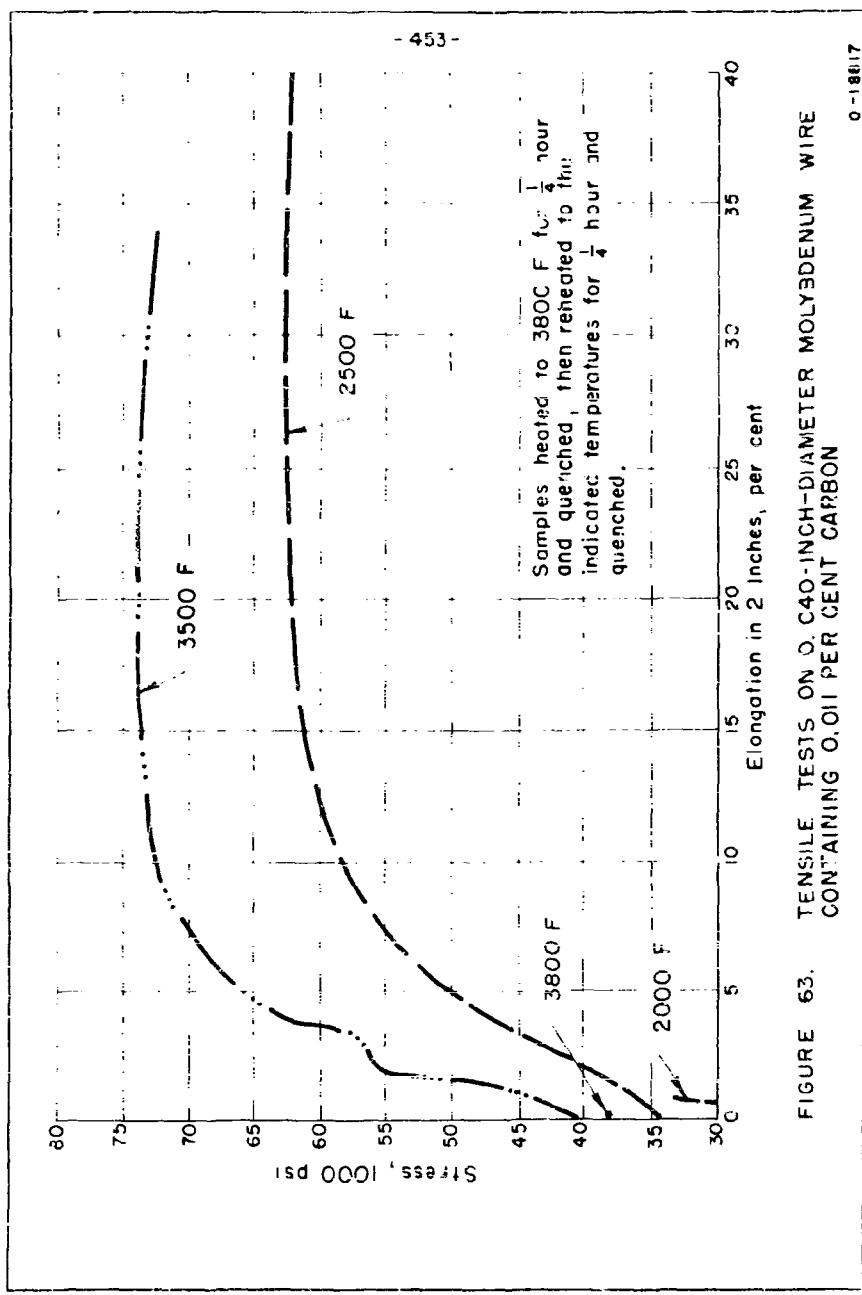
FIGURE 63. TENSILE TESTS ON 0. C40-INCH-DIAMETER MOLYBDENUM WIRE CONTAINING 0.011 PER CENT CARBON

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TABLE 38. TENSILE-TEST AND BEND-TEST DATA ON HEAT-
TREATED 0.040"-DIAMETER MOLYBDENUM WIRE

Temperature of Initial Heat Treatment, °F.	Reheat Temperature, °F.	Time at Reheat Temperature in Minutes*	Bend Angle	Ultimate Tensile Strength, p.s.i., $\varepsilon = 0.0005$ sec.$^{-1}$	Per Cent Elongation (In 2")	Per Cent Reduction in Area	Per Cent Carbon
2000°	None	15	90°**	91093.3	21.5	75.0	0.002
2500°	None	15	90°**	69531.3	34.7	60.9	0.002
3000°	None	15	90°**	56015.6	38.6	57.8	0.002
3300°	None	15	90°**	55468.8	40.5	54.4	0.002
3500°	None	15	90°**	64043.8	34.5	23.4	0.002
3600°	None	15	78°	57812.5	3.8	4.9	0.002
3700°	None	15	20°	43750.0	0.6	2.5	0.002
3800°	None	15	62°	47812.5	2.0	0	0.002
3600°	2000°	15	9°	33593.8	0.5	0	0.002
3800°	2500°	15	90°**	62109.4	7.5	7.4	0.002
3800°	3000°	15	90°**	54375.0	4.5	4.9	0.002
3800°	3300°	15	90°**	54687.5	3.9	4.9	0.002
3800°	3500°	15	90°**	64375.2	39.7	64.0	0.002
3800°	3600°	15	63°	35468.8	1.5	2.5	0.002
3800°	3700°	15	4°	30859.4	0	0	0.002
3800°	3800°	15	3.5°	26953.1	0	0	0.002
3800°	None	15	4°	34575.0	0	0	0.002

* Same time used in reheating cycle as used in original heat treatment.
** 90° is limit of bend angle for Olsen Stiffness Tester.
† to fracture.

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TABLE 39. TENSILE-TEST AND BEND-TEST DATA ON HEAT-TREATED 0.040"-DIAMETER MOLYBDENUM WIRE

Temperature of Initial Heat Treatment, °F.	Reheat Temperature, °F.	Time at Reheat Temperature in Minutes*	Bend Angle	Ultimate Tensile Strength, p.s.i., t = 0.0005 sec.⁻¹	Per Cent Elongation (In 2")	Per Cent Reduction in Area	Per Cent Carbon
3800°	2000°	15	13	34000	0	0	0.011
3800°	2500°	15	90°**	32568	1.0	0.5	0.011
3800°	3000°	15	90°**	78125.0	31.0	47.4	0.011
3800°	3300°	15	90°**	72500.0	31.2	31.9	0.011
3800°	3500°	15	90°**	73360.4	33.7	43.8	0.0?
3800°	3800°	15	4°				0.011
3800°	None	15	4°				0.011
3800°	2000°	60	12.5°	30593.8	1.5	2.5	0.002
3800°	2500°	60	90°**	49533.3	2.0	4.9	0.002
3800°	3000°	60	90°**	59296.9	6.5	7.4	0.002
3800°	3300°	60	90°**	44219.0	12.9	12.1	0.002
3800°	3500°	60	90°**	34511.1	0.5	1.5	0.002
3800°	3600°	60	90°**	64297.1	17.8	14.9	0.002
3800°	3700°	60	90°**	57968.8	5.0	4.9	0.002
3800°	3800°	60	15°	38828.1	34.3	94.2	0.002
3800°	None	60	90°**	56015.6	4.4	7.4	0.002

* Same time used in reheating cycle as used in original heat treatment.
** No fracture. 90° is limit of bend angle for Olsen Stiffness Tester.

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about the same degree and that the embrittlement in both cases is associated with heating to within the temperature range of 3600 to 3800°F. Consequently, it would appear that carbon is not the cause of the embrittlement observed.

It is interesting to note that all these samples appear to be single phased when examined at 1200 diameters. Therefore, if precipitation occurred during the reheating operation, as would be expected in the material containing 0.011 per cent C, it was in a submicroscopic form, since careful microscopic examination and fracture examination failed to reveal the presence of a second phase.

While performing the above experiments, it was found that the time between heat treatment and testing was important in determining whether or not the material was ductile. If 0.002 per cent C wire was quenched from 3800°F. after 1 hour at temperature and allowed to age at room temperature for 15 days, it became completely brittle. But, if tested shortly after heat treatment, it was found to exhibit some ductility in the bend test.

Since the aging characteristic was not realized when this program was set up, the specimens utilized in the aging graphs and tables do not comprise a regular schedule of testing intervals. Also, it will be noticed the aging times in Figure 64, which pertain to bend tests vs. aging time, are different from the times used in Table 40, which illustrate the aging characteristics in terms of both the tensile test and the bend test.

At present, the breadth of the quenching temperature range, which will produce room-temperature aging, is not known. However, it appears from the results presented in Table 40 that the aging process may be affected by the time interval it is held at the quenching
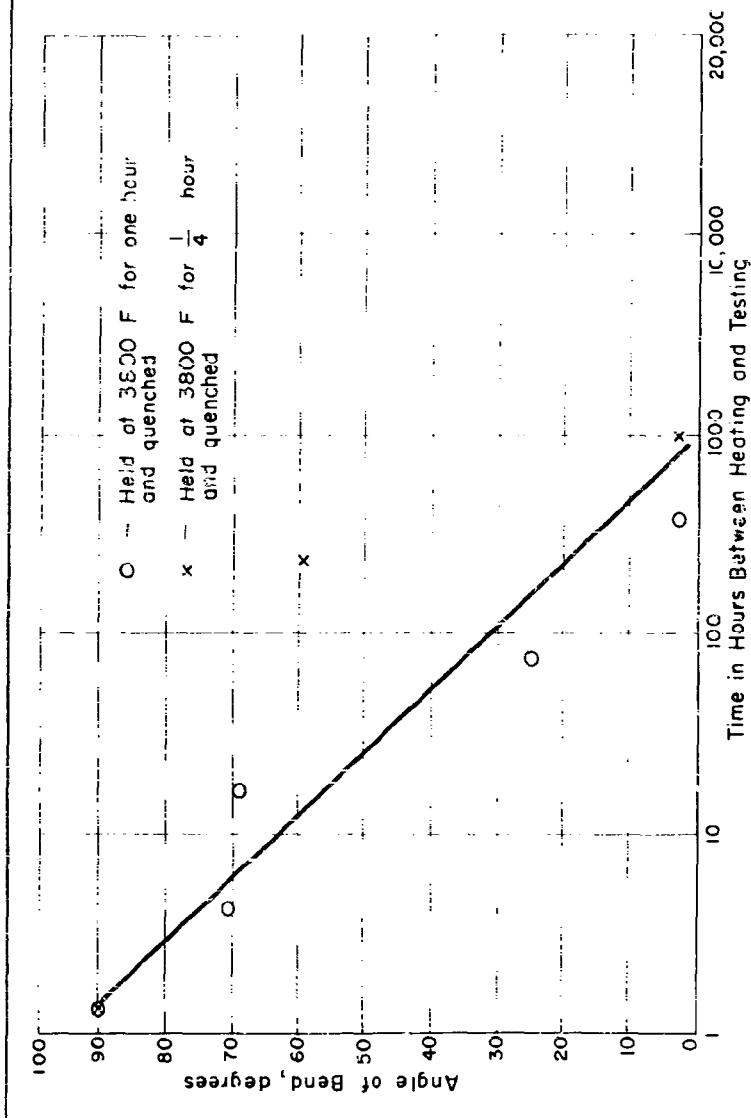
FIGURE 64.   ROOM-TEMPERATURE AGING CHARACTERISTICS OF C.040-INCH-
DIAMETER MOLYBDENUM WIRE CONTAINING O.CO2 PER CENT CARBON

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TABLE 40. PHYSICAL TEST DATA ON 0.040"-DIAMETER MOLYBDENUM WIRE QUENCHED FROM 3800°F., AGED AT ROOM TEMPERATURE

Temp. of Heat Treatment, °F.	Time of Heat Treatment in Minutes	Time Between Heat Treatment and Bend Test in Hours	Bend Angle	Time* Between Heat Treatment and Tensile Test in Hours	Ultimate Tensile Strength, P.s.i. $\varepsilon = 0.0005$ sec.$^{-1}$	Per Cent Elongation (In 2")	Per Cent Reduction in Area	Per Cent Carbon
3800°	60	4	71°	984	37656.3	0	1.0	0.002
3800°	60	24	69°	1008	34375.0	0	1.5	0.002
3800°	60	72	32°	1032	32421.9	0	1.0	0.002
3800°	60	360	5°	1320	30859.4	0.7	0	0.002
3800°	60	360	5°	1344	27343.8	0	1.0	0.002
3800°	15	240	62°	1440	47812.5	2.0		0.002
3800°	15	984	4°	2664	34375.0	0		0.002

* Tensile tests were not arranged to study aging. Bend-test data only should be related to aging.

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temperature. Some variation is noted between samples held at temperature for 15 minutes vs. those held for 1 hour (See Table 40). The longer time at 3800°F. seems to accelerate the room-temperature aging process. This has shown up both in the bend test and the tensile test.

This apparent aging process in molybdenum could explain why the material is ductile if it is given a second heat treatment after quenching from 3000°F. The second heat treatment at 2500°F. to 3500°F., which produced samples capable of showing up to 40 per cent elongation and 50 per cent reduction in area, very likely produces overaging.

The results shown in Figure 64 and Table 40 quite definitely indicate a room-temperature aging process taking place in molybdenum. Apparently, it is still going on to some extent even after 50 to 60 days. Since these effects are caused without noticeable over-all composition change, the cause must be attributed to some solute element, probably N_2, O_2, or H_2.

Future Work

In order to understand fully the results of these ductility studies, it will be necessary to outline critical experiments capable of isolating the known variables. Since this type of planning requires considerable time, probably little experimental time will be devoted to the ductility studies during the coming quarter. It now appears more important to complete the work on the Mo-O system as soon as possible, for it undoubtedly will be of considerable help in planning an intelligent ductility program.

(Data from which this report was prepared are recorded in B.M.I. Notebooks No. 4665, pp. 1-100, and No. 6121, pp. 1-8.)

THE IMPROVEMENT OF THE ROOM-TEMPERATURE
DUCTILITY OF CAST MOLYBDENUM

(K. S. Edwards, E. Eichen, R. B. Fischer,
and J. H. Jackson)

Introduction

It has been known for some time that commercial arc-cast
molybdenum in the as-cast condition is much less ductile than wrought
molybdenum. For this reason, it is necessary at present to use wrought
molybdenum in many applications where using the cast metal would greatly
simplify fabrication. The objective of this section of the molybdenum
program has been to uncover and remove the causes of low ductility in
arc-cast molybdenum in the as-cast condition.

Individual grains of cast molybdenum have, in previous work,
been found to be ductile. However, there is a marked weakness at the
grain boundaries of this material. This weakness results from impurities,
identified as carbides, which tend to collect at grain surfaces. The
present program has been aimed at eliminating these impurities, and thus
raising the ductility, through purification, of the metal.

One simple means of comparing the ductilities of the several types
of molybdenum is a comparison of the temperatures of transition from
ductile to brittle behavior. It is known that, for a given metal and
stress system, there is a linear relation between the logarithm of the
deflection rate and the reciprocal of the absolute temperature of
transition. Such a plot (Figure 69) has been made for a sample of
Westinghouse powder-metallurgy molybdenum which had been swaged and
partially recrystallized, and for a sample of Climax arc-cast molybdenum

in the as-cast condition. This work shows the difference in ductilities between these two types of molybdenum, as well as the variation in ductility of each with temperature and deflection rate. Tests are about to be made to determine this relation for molybdenum of high purity. When these are completed, the effect of purity on the ductility of as-cast molybdenum will have been established.

Experimental Work

Ductility of Westinghouse Powder-Metallurgy Molybdenum

A series of bend tests* was made on a sample of Westinghouse powder-metallurgy molybdenum. This material had been swaged to 0.625-inch-diameter bar stock. Figure 65 shows the microstructure of the molybdenum, which appears to be partially recrystallized. The longitudinal axes of specimens were parallel to the major axes of the grains.

The tests consisted of bending the specimens at selected temperatures at fixed deflection rates. After the specimens had broken, the bend angles were measured. The data obtained from these tests are given in Table 41. By plotting the permanent bend angles against temperatures for the several deflection rates used (Figure 66), it was possible to determine the approximate transition temperature for these deflection rates. Here "transition temperature" is taken to mean that temperature at which ductility, as measured by the permanent bend angle, disappears. This temperature is not well defined, as can be seen from the scatter in the results, shown graphically in Figure 62.

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* This test is the one used regularly in this work. Specimens are 0.250 inch wide by 0.150 inch thick. The span is 0.625 inch. Specimens are simply supported, centrally loaded.

A. Longitudinal section of swaged bar. Murakami's etch
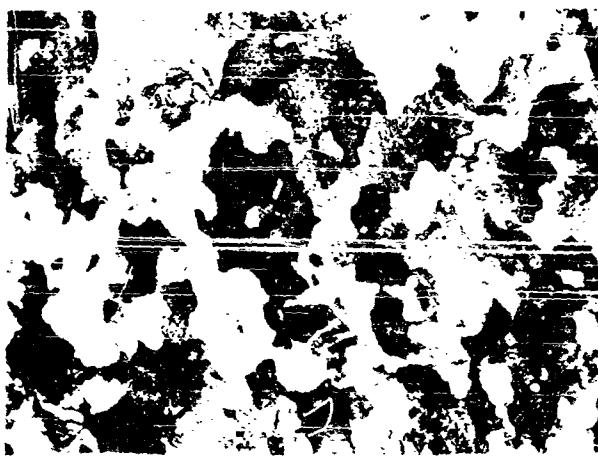
50X 78105

B. Transverse section of swaged bar. Murakami's etch

FIGURE 55. STRUCTURE OF POWDER-METALLURGY MOLYBDENUM SPECIMENS USED IN THE DETERMINATION
OF TRANSITION TEMPERATURES AT VARIOUS STRAIN RATES

TABLE 41. DATA FOR THE DETERMINATION OF THE TRANSITION
TEMPERATURES OF SPECIMENS OF WESTINGHOUSE
POWDER-METALLURGY MOLYBDENUM AT VARIOUS
DEFLECTION RATES

Specimen No.	Platen Speed, In./Min.	Breaking Load, P., Lbs.	Temperature, °C.	Permanent Bend Angle, Degrees
200	1.0	455	-10	0
201	1.0	470	0	0
202	1.0	800	7.5	0
203	1.0	625	12	0
204	1.0	700	22	0
205	1.0	650	24	6
206	0.8	--	22	2
207	0.4	850	22	6
208	0.1	915	-40	0
209	0.1	880	-35	0
210	0.1	730	-30	0
211	0.1	905	-30	3
212	0.1	930	-25	4
213	0.1	920	-25	3
214	0.1	950	-20	3
215	0.1	810	-15	4
216	0.1	820	-10	4
217	0.1	900	-10	0
218	0.1	975	-6	2
219	0.1	900	0	6
220	0.1	950	9	4
221	0.1	1000	22	14
222	0.05	1000	-73	0
223	0.03	770	-41	0
224	0.03	870	-40	0
225	0.03	915	-35	2
226	0.03	965	-29	2
227	0.03	1000	-20	4
228	0.03	850	-14	1
229	0.03	735	-10	2
230	0.03	700	-5	1
231	0.03	950	1	8
232	0.03	900	9	8

TABLE 41. (Continued)

| Specimen No.	Platen Speed, In./Min.	Breaking Load, P., Lbs.	Temperature, °C.	Permanent Bend Angle, Degrees
233	0.01	1000	-74	0
234	0.005	950	-73	0
235	0.005	800	-54	0
236	0.005	800	-52	0
237	0.005	800	-49	3
238	0.005	--	-45	2
239	0.005	950	-35.5	1
240	0.005	900	-35	3
241	0.005	1000	-29	4
242	0.005	800	-23	3
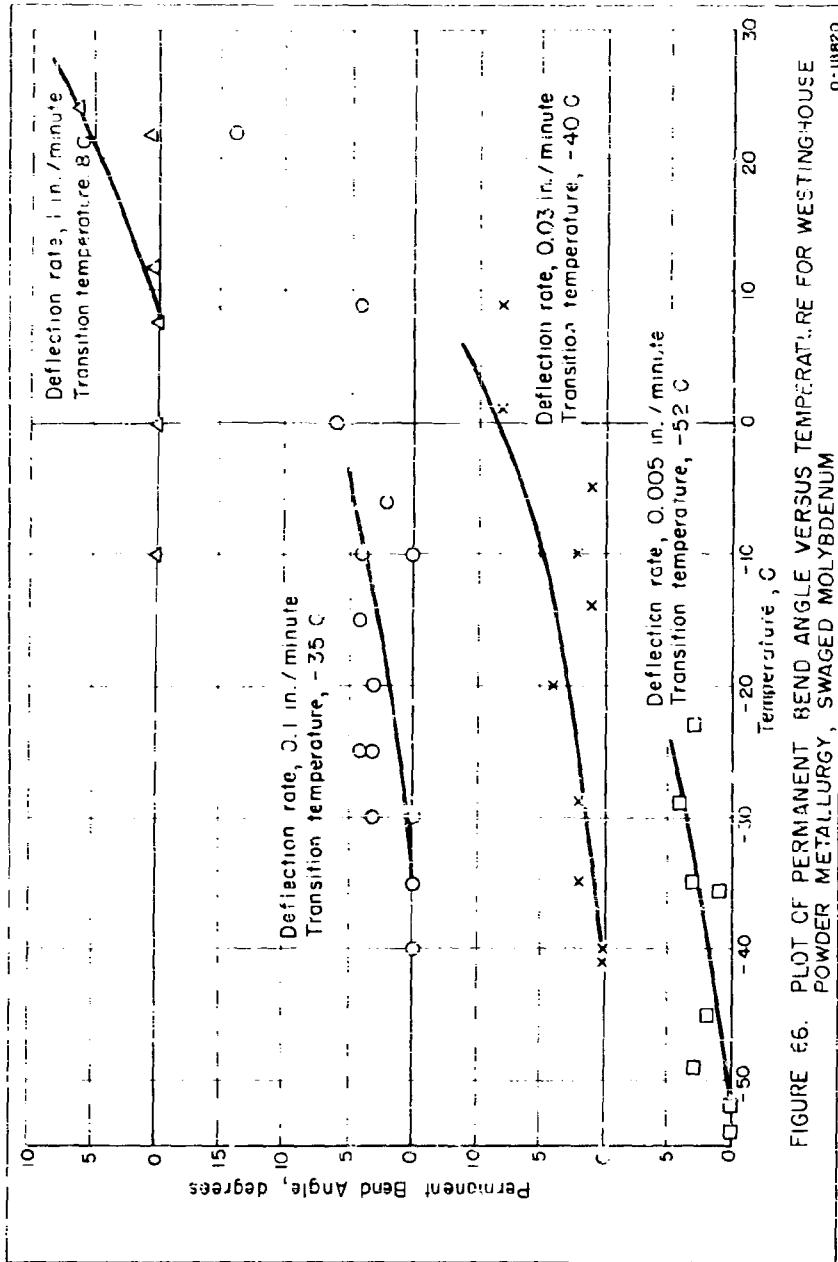
FIGURE 66. PLOT OF PERMANENT BEND ANGLE VERSUS TEMPERATURE FOR WESTINGHOUSE POWDER METALLURGY, SWAGED MOLYBDENUM

Ductility of Climax Arc-Cast Molybdenum

In the Seventh Quarterly Report (pages 384 to 386), the effect
of temperature on the ductility of Climax arc-cast molybdenum (as-cast)
was reported for a deflection rate of 0.005 inch per minute. The
transition temperature for transverse-grain specimens at this deflection
rate was found to be about 150°F. (66°C.). This is the only transition
temperature for transverse-grain specimens of arc-cast molybdenum avail-
able to date.

The transition temperature at a 0.005-inch-per-minute deflection
rate for longitudinal-grain specimens was reported to be -22°F. (-30°C.).
The transition temperature at a deflection rate of 0.04 inch per minute
has recently been found to be about 37°F. (+3°C.). The data used for
establishing this point are shown in Table 42, the plot in Figure 67.

The room-temperature, deflection-rate sensitivity of Climax arc-
cast longitudinal-grain specimens was also reported in the Seventh
Quarterly Report (pages 389 and 390). The "transition deflection rate"
was found to be about 0.24 inch per minute.

These results are shown graphically in Figure 69.

Figure 68 is a photomacrograph of a typical longitudinal-grain
specimen from Climax Ingot 447.

Discussion

The Arrhenius-type plot in Figure 69 is a simple expression of
the comparative ductilities of the Westinghouse powder-metallurgy molyb-
denum and the Climax arc-cast material. It shows at a glance that the
powder-metallurgy metal remains ductile under more severe embrittling
conditions. This can be attributed to differences in amount and

TABLE 42. DATA FOR THE DETERMINATION OF THE TRANSITION
TEMPERATURE OF LONGITUDINAL-GRAIN SPECIMENS
OF CLIMAX ARC-CAST MOLYBDENUM AT 0.04-INCH-
PER-MINUTE DEFLECTION RATE

| Specimen No.	Breaking Load, P., Lbs.	Temperature, °C.	Permanent Bend Angle, Degrees
9	950	5	13
48	950	4	15
56	450	3	0
57	605	3	0
19	690	0	0
14	730	-3	0
14X	700	-7	0
Q	595	-20	0
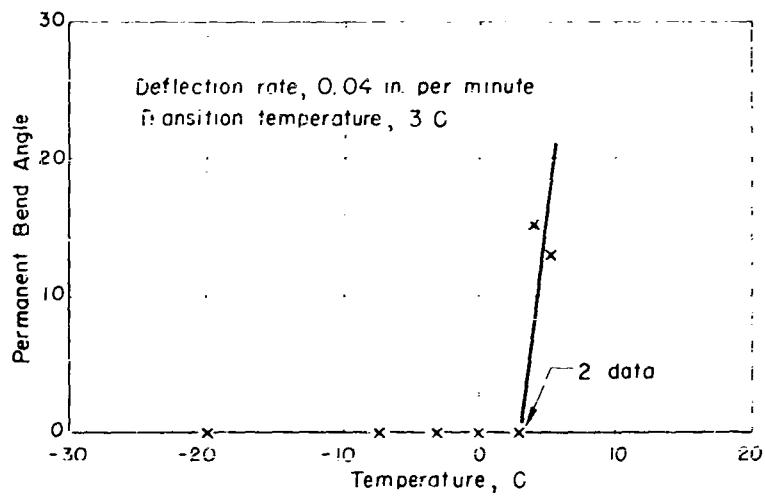
FIGURE 67. PLOT OF PERMANENT BEND ANGLE VERSUS
TEMPERATURE FOR LONGITUDINAL-GRAIN
MOLYBDENUM SPECIMENS FROM CLIMAX
INGOT 447
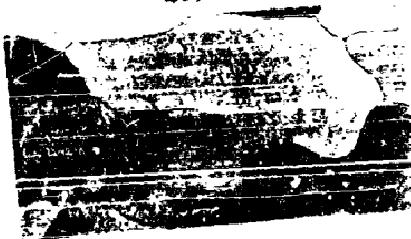
a. Transverse section of specimen. Note small number of grains, about 20.

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10X
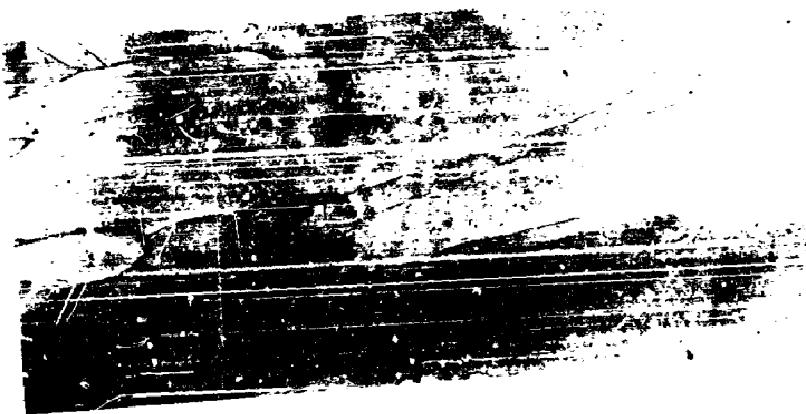
Murakami's Etch

b. Longitudinal section of specimen. Note elongated grains.

FIGURE 68. TYPICAL "LONGITUDINAL" SPECIMEN FROM CLIMAX INGOT 447
(Long Axes of Grains Parallel to Long Axis of Specimen)
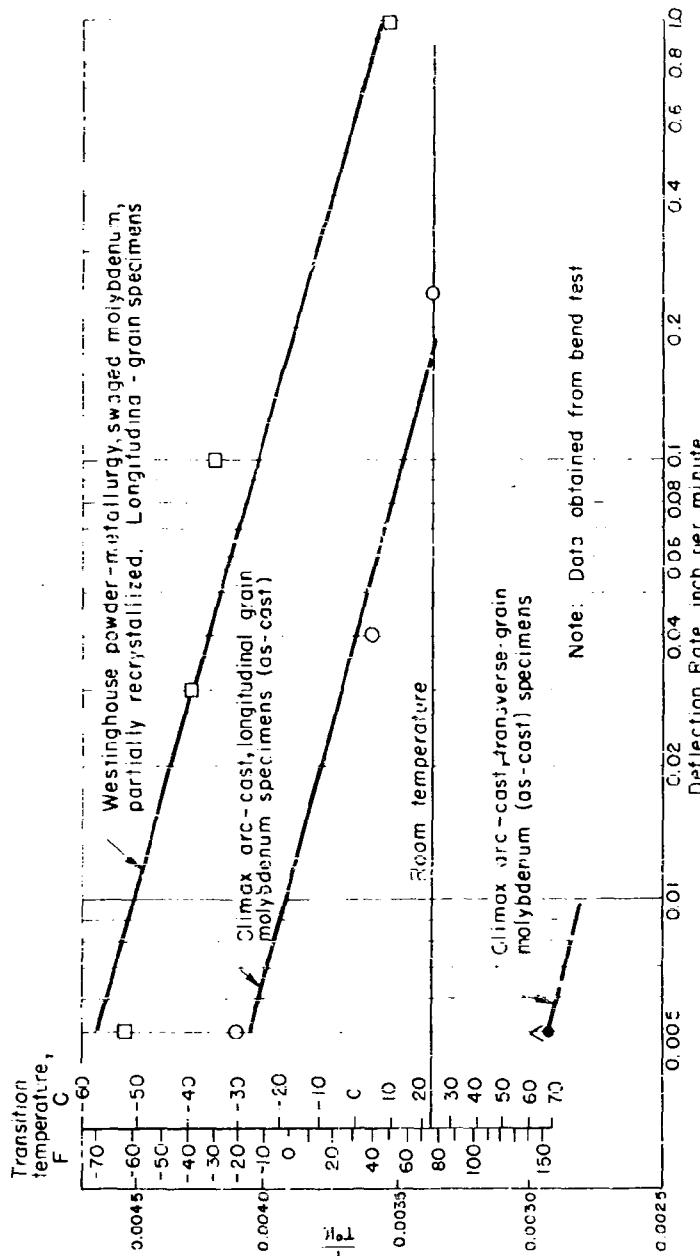
FIGURE 69. ARRHENIUS-TYPE PLOT SHOWING BOUNDARY BETWEEN DUCTILE AND BRITTLE BEHAVIOR IN TEMPERATURE DEFLECTION-RATE DOMAIN FOR SEVERAL TYPES OF MOLYBDENUM SPECIMENS

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distribution of impurities and degree of prior working. The transverse-grain arc-cast molybdenum specimens are shown to be less ductile than the longitudinal-grain specimens. This is owing to the stress-raising effect of carbides at the grain boundaries, which, in the transverse-grain specimens, are subjected to higher normal stresses.

If it is found that the lines representing the frontiers between ductile and brittle behavior for various types of molybdenum consistently have the same slope, it will be a simple matter to determine the frontier for some new type. The transition temperature at some convenient deflection rate will suffice to locate the line.

One must bear in mind that the information presented in Figure 69 is gathered from bend test-data. The correlation between transition temperatures obtained by this means and those found from other tests has not yet been ascertained.

Future Work

Tests are about to be started for determining the boundary between ductile and brittle behavior for high-purity, arc-cast molybdenum in the as-cast condition. This boundary is also to be obtained for Climax arc-cast molybdenum which has been forged, rolled, and annealed.

Analytical work and some experimental work is contemplated for determining the strain-rate, deflection-rate relationship which exists in the bend test used in this work. This will make it possible to predict the tension-test behavior of the various types of molybdenum for which bend-test data are available.

A specimen of triple-melted high-purity arc-cast molybdenum to which carbon was added and one which was melted in a low pressure of high-purity hydrogen (on the third melt) are now ready for testing to determine the effects of these specific elements on ductility.

(The data for this report are recorded in Battelle Laboratory Record Book No. 5588, pp. 33-34, 37-38.)

ANELASTIC STUDIES OF MOLYBDENUM

(R. Maringer, G. T. Muehlenkamp, and A. D. Schwope)

Introduction

The aim of the anelastic studies of molybdenum is to determine the effects of impurities on the internal friction of this metal. The impurities have, at present, been arbitrarily limited to C, N, O, and H. A thorough study of these elements in relation to the internal friction of molybdenum should provide information from which we can determine solid solubilities and other properties of molybdenum.

Test results have indicated that impurities affect the internal friction as the temperature and as the shear stress are varied. Thus, there are two tools with which to work, either or both of which may open the door to the solution of the brittleness problem in molybdenum.

Apparatus

The apparatus for measuring the internal friction is the same as described in the Seventh Quarterly Report, with one exception. The system was modified to permit the use of a refrigeration unit to study specimens at temperatures below room temperature. Temperatures as low as $-28°F$. can be obtained. Further revision of the refrigeration unit may lower this limit.

Since the need arose for specimens quenched from various temperatures under various conditions, equipment was built to carry out this work. The specimen is held between two clamps in a glass tube and resistance heated. The tube can be evacuated or flooded with a gaseous

atmosphere at pressures up to one atmosphere. A purification train using titanium chips at 1560°F. prepares argon for use as an atmosphere. Slight changes will permit the use of other atmospheres as desired.

The temperature of the resistance-heated wire is measured by means of an L.and N.optical pyrometer. Since these measurements are not made under black-body conditions, a correction factor must be added to the readings. True temperatures are computed from brightness temperatures as read from the pyrometer by means of Wien's equation:

$$\log_e C_T = \frac{C_2}{T} \quad \frac{1}{T} - \frac{1}{S_2}$$

where C_T = emissivity for wave length used,

$\quad C_2$ = Wien constant = 14330_u deg.,

$\quad T$ = wave length used,

$\quad T$ = true temperature,

$\quad S$ = brightness temperature.

Another correction factor, obtained experimentally, must be added for the loss of radiation due to passage of the rays through the walls of the glass tube.

Experimental Work

Extensive work was done in trying to duplicate the internal-friction curve as shown in the Seventh Quarterly Report. Several specimens showed indications of a peak in the 500°F. to 600°F. temperature range, but no distinct peak of any size was found. The shear moduli of the various wires varied slightly, from 16.0 x 10⁶ p.s.i. to 18.3 x 10⁶ p.s.i. at room temperature, but there are as yet insufficient data from

which to draw any conclusions.

The absence of a peak in the internal-friction curve suggested the possibility that there was a room-temperature aging effect which changed the structure of the wire to such an extent that the peak was lost. Work done in other departments indicated that a specimen quenched from a certain temperature range would be fairly ductile immediately after quenching, but would become quite brittle after several days. To investigate this possibility, equipment was set up to heat treat specimens and conduct tests immediately after quenching.

Specimens of molybdenum wire having a known content of 0.005 per cent carbon were taken as received from Westinghouse Corporation and quenched in a purified argon atmosphere from temperatures ranging from 3220°F. to 4560°F. after twelve minutes at temperature. Bend tests were run on each specimen within one-half hour of the quench. The majority of the tensile tests were run within two hours after quenching. The results of the tests are presented in Table 43. A graph of tensile strength plotted against quenching temperature (Figure 70) shows a great change in the tensile properties over the temperature range investigated. Wires quenched from between 3220°F. and 3700°F. have a tensile strength of about 60,000 p.s.i. Specimens quenched from above 3700°F. gradually decrease in tensile strength until, at 4300°F., a minimum of about 20,000 p.s.i. is found. Bend tes s showed that, as the tensile strength decreased, brittleness increased. Above 4300°F., the tensile strength rose to about 50,000 p.s.i.

TABLE 43. VARIATION OF PROPERTIES OF MOLYBDENUM QUENCHED IN AN ARGON ATMOSPHERE WITH QUENCHING TEMPERATURE

Specimen Number	Temperature in °F.	Time at Temp. in Min.	Per Cent Reduction of Area	Per Cent Elongation	Tensile Strength	Aging Time	Angle of Bend
19	3220	12	30	37	84,300	$\frac{1}{2}$ hr.	90°
13	3580	12	19	—	79,200	$\frac{1}{2}$ hr.	90°
13	3580	—	—	—	—	52 hrs.	90°
18	3640	12	40	44	81,500	$\frac{1}{2}$ hr.	90°
18	3640	—	—	—	—	120 hrs.	90°
14	3710	12	13.5	—	84,200	$\frac{1}{2}$ hr.	90°
14	3710	—	—	—	—	120 hrs.	90°
15	3770	12	—	—	60,500	$\frac{1}{2}$ hr.	51°
15	3770	—	—	—	—	77 hrs.	42°
16	3840	12	—	—	60,100	$\frac{1}{2}$ hr.	90°
16	3840	—	—	—	—	72 hrs.	90°
17	3900	12	—	—	37,800	$\frac{1}{2}$ hr.	28°
17	3900	—	—	—	—	72 hrs.	30°
11	3960	12	—	—	34,600	$\frac{1}{2}$ hr.	8°
11	3960	—	—	—	—	$\frac{1}{2}$ hr.	16°
11	3960	—	—	—	—	$\frac{1}{2}$ hr.	11°
10	4100	12	4	—	27,900	$\frac{1}{2}$ hr.	4°
7	4230	12	—	—	22,300	$\frac{1}{2}$ hr.	2°
8	4290	12	—	—	21,100	$\frac{1}{2}$ hr.	3°
6	4360	12	15	—	50,500	$\frac{1}{2}$ hr.	90°
6	4360	—	—	—	—	44 hrs.	90°
6	4360	—	—	—	—	8 days	90°
5	4410	12	—	—	50,900	$\frac{1}{2}$ hr.	90°
5	4410	—	—	—	—	96 hrs.	90°
9	4560	12	—	—	41,000	$\frac{1}{2}$ hr.	90°
9	4560	—	—	—	—	148 hrs.	90°

All specimens are Mo containing 0.005 per cent carbon and were quenched in an atmosphere of high-purity argon, further purified by passing over titanium chips at 1500°F. Head travel on all tensile tests was 1/8 inch per minute. Bend tests were run on a Tinius-Olsen Stiffness Tester.
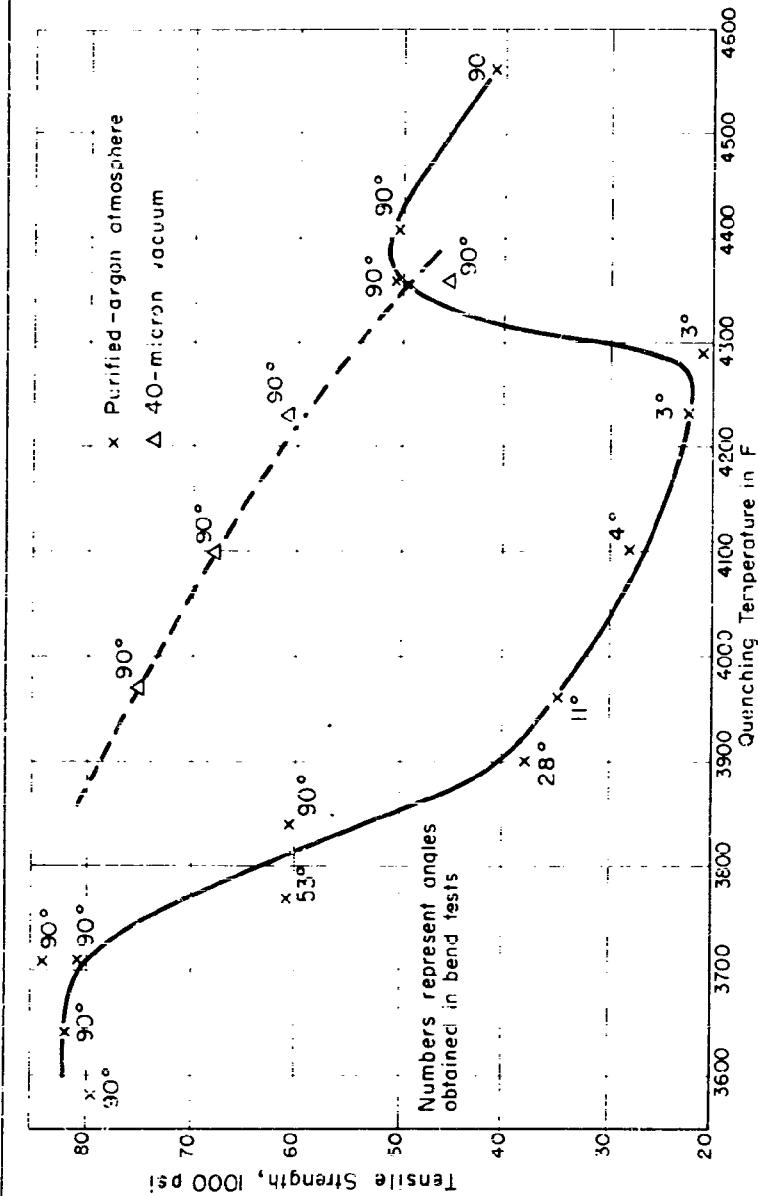
FIGURE 70. VARIATION OF TENSILE STRENGTH WITH QUENCHING TEMPERATURE OF MOLYB-
DENUM CONTAINING 0.005 PER CENT CARBON

Since it is thought that impurities in molybdenum influence ductility, the graph indicates that, as the quenching temperature increases, impurities are being taken into solution, either from the wire itself, or from the surrounding atmosphere. Above 4300°F. a degassing effect may be reducing the impurity content, thereby increasing the ductility. If this is true, a wire heat treated in a vacuum would eliminate the possibility of absorbing impurities from the atmosphere and at the same time hasten the degassing process.

In view of this, four specimens were heated in a vacuum of about 40 microns and quenched from temperatures of 3970°F., 4100°F., 4230°F., and 4360°F. after 15 minutes at temperature (Table 44). Although the tensile strength decreased as the quenching temperature increased, the brittleness as noticed on the bend tests of the previous specimens was completely absent, as was the dip in the tensile strength curve between 3700°F. and 4300°F. This purification, if such it is, will be checked by metallographic and chemical analyses. Tests can then be run to determine the time-temperature relationships of this purifying process.

At the higher temperatures of 4230°F. and 4360°F., considerable vaporization of the specimen was noted. The diameter of the wire heated to 4360°F. diminished from 0.040 inch to 0.036 inch after 10 minutes at temperature.

Bend tests on specimens heat treated in both the purified argon atmosphere and in the vacuum have not given any indication of quench aging after periods of up to one week after quenching.

TABLE 44. VARIATION OF PROPERTIES OF MOLYBDENUM QUENCHED
IN A VACUUM WITH QUENCHING TEMPERATURE

| Specimen Number	Temperature in °F.	Time at Temp. in Min.	Per Cent Reduction of Area	Per Cent Elongation	Tensile Strength	Aging Time	Angle of Bend
23	3970	15	12	16	74,800	½ hr.	90°
23	3970	--	--	--	--	6 days	90°
22	4100	15	6	9	67,600	½ hr.	90°
22	4100	--	--	--	--	7 days	90°
21	4230	14	4	6	60,500	½ hr.	90°
21	4230	--	--	--	--	7 days	90°
24	4360	10	?	4	45,200	½ hr.	90°
24	4360	--	--	--	--	6 days	90°

All specimens on Mo containing 0.005 per cent carbon were
quenched in a vacuum of approximately 40 microns. Head travel on all
tensile tests was 1/8 inch per minute. Bend tests were made on a Tinius-
Olsen Stiffness Tester.

The vacuum system used for these tests is being improved. The system is being changed to include a diffusion pump. With a lowering of pressure, the danger of gaseous impurities, diffusing into the system will be greatly lessened.

Internal-friction tests were run on two wire specimens, one containing 0.011 per cent carbon, the other, 0.005 per cent carbon. The 0.011 per cent carbon wire had been quenched twice from 3800°F. in a purified argon atmosphere after 15 minutes at temperature. At room temperature (71° - 80°F.), Q^{-1} (internal friction) values ranged from about 0.0010 at a shear stress of about 75 p.s.i. to about 0.0021 at a shear stress of about 1000 p.s.i. (See Figure 71.) Several tests were made on the same specimen, alternating tests at room temperature with tests at -28°C. The slope of the graph was the same for all tests. Successive tests at room temperature yielded successively lower values of internal friction.

Tests of the 0.005 per cent carbon wire (See Figure 72) at 73°F. gave a Q^{-1} value at low stresses which was practically the same as that of the 0.011 per cent wire. There was, however, very little change in the Q^{-1} value as the shear stress was increased. A second test yielded lower Q^{-1} values, but the graph still had the same slope.

The lowering of the Q^{-1} values with successive tests is probably due to the relief of internal stresses. One of the major causes of micro stresses is the retention of elements in solid solution beyond the equilibrium concentration. This phenomenon may then be interpreted as a precipitation process. Further controlled testing will clarify this point. This variation presents an additional method of detecting changes in a material associated with impurity elements.
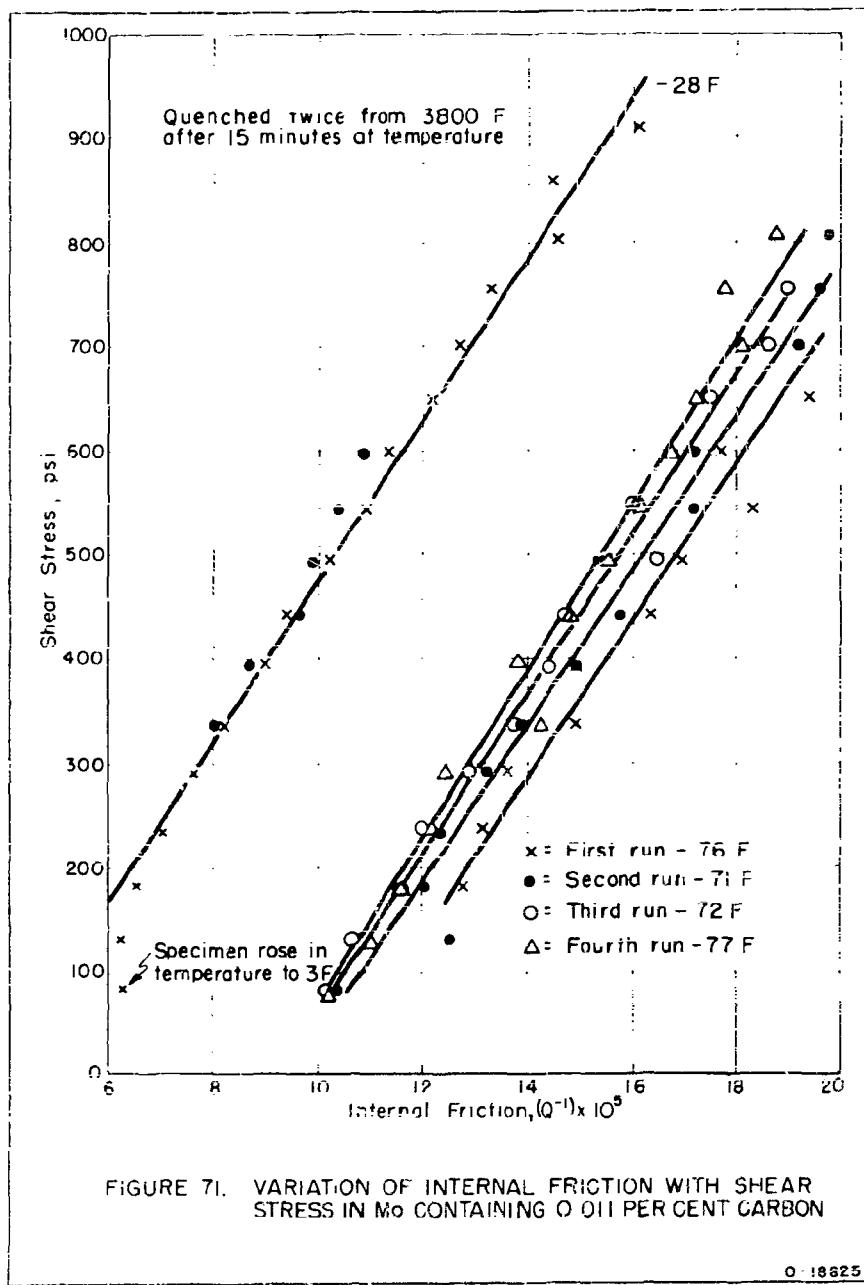
FIGURE 71. VARIATION OF INTERNAL FRICTION WITH SHEAR
STRESS IN Mo CONTAINING 0 011 PER CENT CARBON

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FIGURE 72. VARIATION OF INTERNAL FRICTION WITH SHEAR STRESS IN Mo CONTAINING 0.005 PER CENT CARBON

0-18826
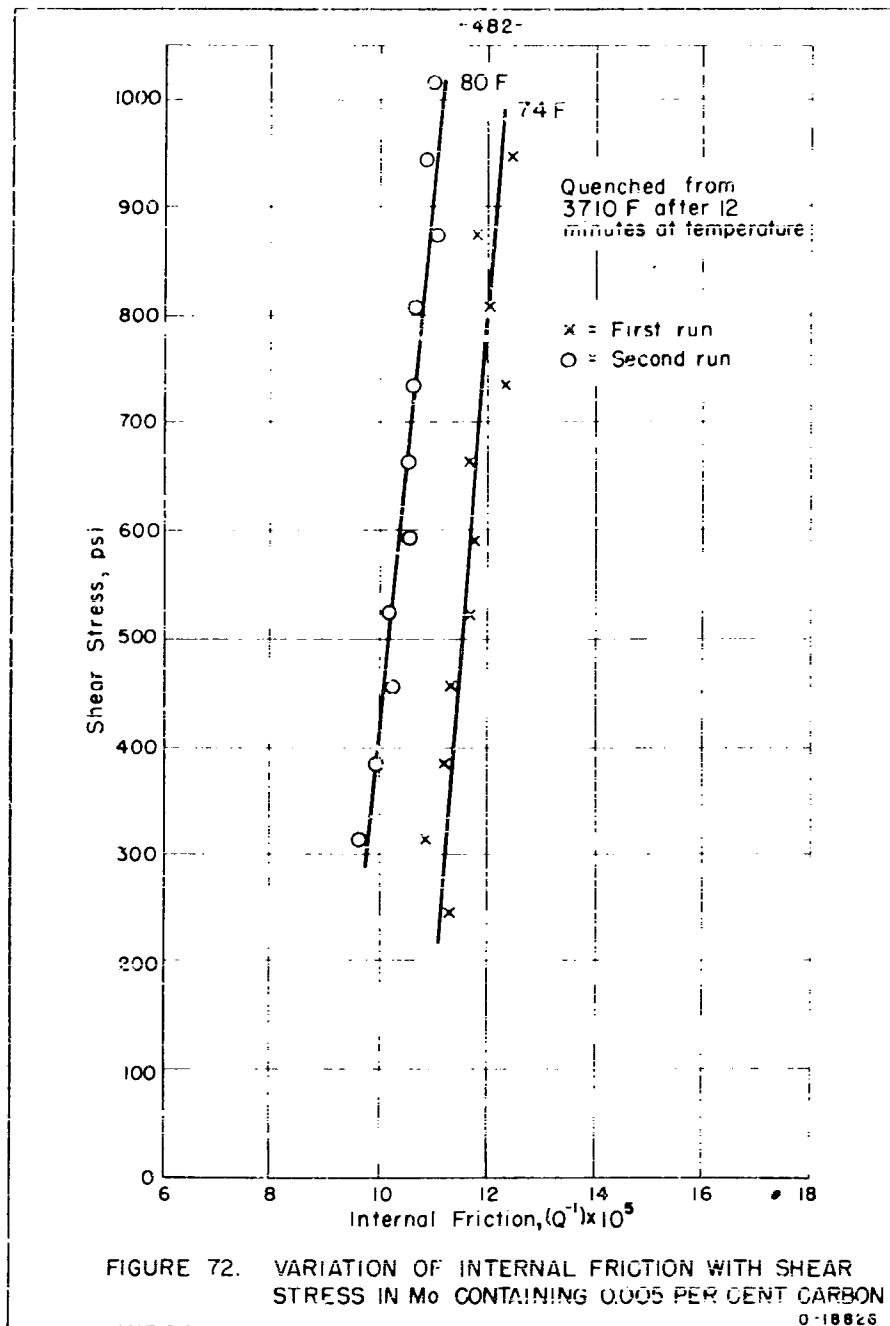
Summary

Efforts were made to find a peak in the internal friction vs. temperature curve of molybdenum due to interstitial elements in solid solution, but the tests showed negative results. To investigate other effects of the interstitial elements, the internal-friction apparatus was modified to permit testing below room temperature and other apparatus was built to heat treat molybdenum wire at any temperature in any atmosphere or in a vacuum. Wire quenched from various temperatures after being heat treated in a purified argon atmosphere showed a definite dependence of tensile strength and bend angle on the quenching temperature. The tensile strengths of wires quenched in a vacuum also indicated a dependence on the quenching temperature. It is thought that heat treating the wire in a vacuum tends to degas the specimen, rendering it somewhat more ductile.

Internal-friction tests at and below room temperature show the internal friction to be linearly dependent on stress at low stress amplitudes. A variation in the slope of the Q^{-1} vs. stress curve was found and will be investigated with respect to its dependence on the impurity content of the wire.

Future Work

Future work will consist of determining if specimens heated in a vacuum at high temperatures are being purified. If so, degassed specimens can be impregnated with large amounts of only one impurity. These wires will then be subjected to tension, bend, and internal-friction tests, as well as chemical and metallographic analyses.

The investigation has been planned to determine the effect of individual elements on aging as well as on ductility in the absence of aging. Nitrogen has tentatively been decided upon as the first impurity to investigate. Results of these tests can then be used as criteria for the study of the effects of C, O, and H on the internal friction of molybdenum.

(Data from which this report is written may be found in B.M.I. Record Book No. 5448, pp. 25-48.)

REFERENCES

(1) Bueckle, H., "Surface Protection of High-Melting Metals to Increase Their Resistance to Scaling", Metallforschung, V. 1, pp. 81-86 (1946); abstracted in Metal Progress, V. 59, pp. 288-290 (1951).

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